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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

A New Method of Expressing the Formulæ of Line Spectra Alfred Lartigue (*Compt. rend.*, 1919, **169**, 914—915).—In place of the general formula $10^8/\lambda = N_0(1/p^2 - 1/q^2)$ waves per cm., the author proposes to use the formula $\lambda_m = (4 \times 10^8/N_0)(p/2)^2[2/p + 1/m - 1/(m+2p)]$ Ångströms, where $m = q - p$. W. G.

Luminous Phenomena Observed in the Neighbourhood of a Plate of Graphite raised to a High Temperature by means of an Electric Current. G. A. Hemsalech (*Compt. rend.*, 1919, **169**, 915—918).—A sheet of graphite 0·95 mm. thick had its upper surface covered with a thin layer of carborundum powder, and an electric current was passed through it. As the temperature of the plate increased, when it became incandescent, yellow vapours appeared above the plate and were carried upwards by the air convection currents. When the temperature of the plate reached 2500—2700°, the space bounded by the plate and the air convection currents became filled with a luminous vapour which gave a spectrum composed of rays and bands, whilst the yellow vapours became blue and also luminous, and gave a continuous spectrum. When the temperature of the plate reached 3000°, a red fringe appeared on its lower surface and in contact with it, and was formed by the passage of an electric current through the conducting vapours. Its position could be controlled

αγδ-Tribromopentane from αε-Dibromopentane. Julius von Braun and Georg Kirschbaum. (*Ber.*, 1919, **52**, [*B*], 1713—1716).—Tribromides of the type

$$CH_2Br{\cdot}CHBr{\cdot}[CH_2]_n{\cdot}CH_2Br$$

react with magnesium to form Grignard compounds of the formula $CH_2{:}CH{\cdot}[CH_2]_n{\cdot}CH_2{\cdot}MgBr$, which may be converted into iodides, $-CH_2I$, by means of iodoacetonitrile (see A., 1912, i, 434). From the magnesium compound or the iodide it would be possible to synthesise substances containing unsaturated alkyl groups, and consequently the authors have sought for methods whereby the tribromides of the desired type might be prepared conveniently, and have found the most promising material to be the αω-dibromoparaffins. These only react with bromine in the presence of iron wire, and then the reaction is vigorous and so much bromine is lost that the process must be repeated. The position of the bromine atoms in the product is not what might be expected. In the case of αε-dibromopentane, for example, the product is *αγδ-tribromopentane*, $CH_2Br{\cdot}CH_2{\cdot}CHBr{\cdot}CHBr{\cdot}CH_3$, a stable oil with spicy odour, b. p. 120—124°/11 mm., and not the expected αδε-compound, b. p. 128—132°/12 mm. (A., 1918, i, 164). Its constitution is proved by converting it into Δ$^{\gamma}$-hexenoic acid,

$$CHMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H,$$

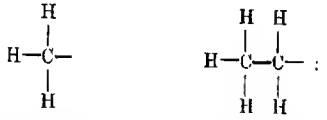
through the Grignard reaction. J. C. W.

Method of Producing Methyl Alcohol from Alkyl Formates. J. A. Christiansen (U.S. Pat. 1302011).—Methyl alcohol is produced by treating an alkyl formate with hydrogen in the presence of a catalyst, for example, partly reduced copper at 180°, $H{\cdot}CO_2Me + 2H_2 = 2MeOH$. The methyl formate may be produced by leading carbon monoxide and methyl alcohol vapour, at high pressure, over solid sodium methoxide, or by passing carbon monoxide into a solution of sodium methoxide in methyl alcohol, $CO + Me{\cdot}OH = H{\cdot}CO_2Me$.

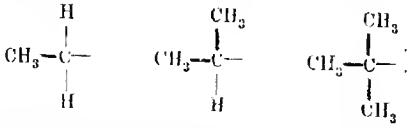
The Distillation of Aqueous Solutions of Ethylene Monochlorohydrin. J. Bancelin and G. Rivat (*Bull. Soc. chim.*, 1919, [iv], **25**, 552—560).—The distillation of commercial aqueous solutions of ethylene monochlorohydrin gives a distillate passing at a fixed point (97·85°/760 mm.) containing 42% of the monochlorohydrin, independent of the concentration of the original solution. These results are confirmed by figures obtained with solutions made from the pure monochlorohydrin, except that in this case the distillate has a content of 41% of monochlorohydrin. Such a distillate has D^{15} 1·094. There is no direct evidence of the formation of a hydrate. W. G.

Pinacolin Transformations. V. The Varying Affinity Demands of Aliphatic Radicles. Hans Meerwein (*Annalen*, 1919, **419**, 121—175).—It has been shown that the pinacolin transformation is caused by the direct loss of a hydrogen atom and a hydroxyl group from the molecule of the glycol, and subsequent

migration of a radicle. With symmetrical glycols, it is a matter of indifference as to which hydroxyl group is eliminated, but with unsymmetrical glycols of the type $OH\cdot CR_2\cdot CR_2'\cdot OH$, two distinct products, $CR_2R'\cdot CO\cdot R'$ and $CRR_2'\cdot CO\cdot R$, result, according as the one or the other hydroxyl group is expelled. In general, the less firmly attached group will be mainly or entirely eliminated, and the nature of the pinacolin produced therefore throws considerable light on the relative strength of the attachment of the hydroxyl groups. Since, however, these may be regarded as being bound by the residue of the affinity of the carbon atom which is not required by the alkyl groups, a direct method of comparing the affinity demands of various alkyl groups is provided. A series of comparisons by this method is described in the present communication. It is found that the valency requirements of the normal alkyl groups diminish with increasing number of carbon atoms; this diminution, however, is not continuous, but exhibits a periodicity of such nature that the alkyl groups with an odd number of carbon atoms have greater affinity demands than those with an even number of carbon atoms. This apparent anomaly is, however, readily explained when the groups are formulated in the following manner, in which the light and heavy strokes represent the different affinity demands:



If now, the *n*-propyl group is considered as formed by the displacement of a hydrogen atom in methyl by the ethyl radicle, it is seen that it must have a greater valency requirement than the ethyl group, since the demand of the latter is less than that of the methyl group. By a similar line of reasoning, it is seen that the affinity requirement must diminish uniformly in the case of alkyl groups with side-chains



and this appears to be the case as far as the evidence available allows conclusions to be drawn.

[With Adolf Schweinheim.]—The action of magnesium *n*-propyl bromide on methyl dimethylglycollate (compare Parry, T., 1911, 99, 1171) leads to the formation of a mixture of *as*-dimethyldi-*n*-propylethylene glycol and dimethyl-*n*-propylethylene glycol, the Grignard compound behaving in part as a reducing agent and evolving propylene. The b. p.'s of the constituents lie so closely together that the substances cannot be separated by fractionation,

and the mixture was therefore submitted to the action of ice-cold concentrated sulphuric acid, whereby propyl *iso*propyl ketone, b. p. 135—136° (semicarbazone, m. p. 119°), and a mixture of the theoretically possible pinacolins were obtained. The latter are conveniently separated and approximately estimated by taking advantage of the great differences in the readiness with which they react with semicarbazide and the widely differing solubilities of the semicarbazones. *αα-Methyldi*-n-*propylacetone* [*methyl α-methyl-α-propylbutyl ketone*], $CMePr_2{\cdot}COMe$, is an oil with a pronounced camphoraceous odour, b. p. 191·5—192°, D_4^{20} 0·8351, n_D^{20} 1·42927 (*semicarbazone*, coarse needles, m. p. 149—150°), whilst n-*propyl αα-dimethylbutyl ketone*, $CMe_2Pr{\cdot}COPr$, has b. p. 188·5—189°, D_4^{20} 0·8295, n_D^{20} 1·42634 (*semicarbazone*, slender needles, m. p. 104°). The ratio of the amounts of the latter to the former in the mixture is 10:8. A similar ratio (11:8) was obtained by oxidising the mixture with boiling dilute nitric acid and separating the acids formed; in this manner, αα-dimethylvaleric acid, b. p. 105—108°/14 mm., and *α-methyl-α*-n-*propylvaleric acid*, b. p. 118—122°/14 mm., m. p. 43—44°, were obtained. A mixture of *dimethylmonobutylethylene glycol* [*β-methylheptane-βγ-diol*], b. p. 109—113°/10·5 mm., and as-*dimethyldi*-n-*butylethylene glycol* [*β-methyl-γ-butylheptane-βγ-diol*], m. p. 32—32·5°, b. p. 130·5—131°/9 mm., was prepared from magnesium *n*-butyl bromide and dimethylglycollic ester; the latter glycol yielded a mixture of pinacolins, which could be separated and approximately analysed by means of semicarbazide. *Methyl-αα-di*-n-*butylacetone* [*γ-methyl-γ-butylheptane-β-one*] forms a colourless oil with a peculiar, sweet odour, b. p. 107·5—108·5°/14 mm., D_4^{20} 0·8380, n_D^{20} 1·43667 (*semicarbazone*, coarse needles, m. p. 108°), the constitution of which is deduced by its oxidation with dilute nitric acid to *α-methyl-α*-n-*butylvaleric acid*, a viscous oil, b. p. 158—159°/18 mm. n-*Butyl* tert.-*heptyl ketone* [*εε-dimethyldecane-ζ-one*] is a colourless, mobile oil, b. p. 105·5—106·5°/15 mm., D_4^{20} 0·8323, n_D^{20} 1·43420, and is transformed by nitric acid into *αα-dimethylvaleric acid*, b. p. 120—122°/15 mm. The ratio of butyl *tert.*-heptyl ketone to methyldibutylacetone in the pinacolin mixture is approximately 7:4.

The investigation has been extended to tetraethylethylene glycol, since, according to Kohn (A., 1905, i, 928) and Samec (A., 1907, i, 746), this substance does not yield a true pinacolin, but an isomeric alkylene oxide. This supposition is based on the facts that it does not yield an oxime and is indifferent towards zinc ethyl. It is now shown however, that the glycol actually yields ethyl *tert.*-heptyl ketone [γγ-diethylhexane-δ-one], b. p. 194—195°, D_4^{20} 0·8501 n_D^{20} 1·43519, as is shown by the formation of αα-diethylbutyric acid, m. p. 38°, b. p. 121—122°/16 mm., $D_4^{99\cdot3}$ 0·9119, $n_D^{99\cdot3}$ 1·42778 (*sodium* salt, leaflets, $+3H_2O$), when the latter is oxidised with dilute nitric acid.

The relative firmness of attachment of the methyl and ethyl groups is further demonstrated in the behaviour of *αα-diphenyl-*

ββ-methylethylethylene glycol [*αα-diphenyl-β-methylbutane-αβ-diol*], which is obtained as a colourless, very viscous oil, b. p. 202°/12 mm., by the action of magnesium phenyl bromide on methyl methylethylglycollate. The glycol is transformed by concentrated sulphuric acid exclusively into *αα-diphenyl-α-ethylacetone* [*γγ-diphenylpentane-δ-one*], coarse leaflets, m. p. 27°, b. p. 179°/11 mm. (*semicarbazone*, slender needles, m. p. 199—200°), the constitution of which is deduced from its conversion by sodium hypobromite into *αα*-diphenylbutyric acid, m. p. 172—173·5°, and from its transformation by soda-lime into *αα*-diphenylpropane, b. p. 274—280°, and acetic acid.

[With FRITZ KREMERS.]—As in previous cases, the action of magnesium *n*-propyl bromide on methyl 1-*cyclo*pentanol-1-carboxylate gave rise to a mixture of "*propyltetramethyleneglycol*" [1-*α-hydroxybutyl*cyclo*pentan*-1-*ol*], $\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C(OH)\cdot CHPr\cdot OH$, and "as-*di*-n-*propyltetramethyleneglycol*" [1-*α-hydroxy-α-propylbutyl*cyclo*pentan*-1-*ol*], $\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C(OH)\cdot CPr_2\cdot OH$, which could not be separated satisfactorily by fractional distillation, and was therefore immediately submitted to the dehydrating action of aqueous oxalic or concentrated sulphuric acids, the products of which were *butyryl*cyclo*pentane*, colourless oil, b. p. 198° (*oxime*, colourless oil, b. p. 135—138°/21 mm., *semicarbazone*, slender needles, m. p. 110—111°), and a mixture of pinacolins, which were separated through their semicarbazones. 1:1-*Dipropyl*cyclo*hexanone* is a colourless oil with an intense odour of peppermint, b. p. 119—120°/17 mm., D_4^{20} 0·9062, n_D^{20} 1·46172 (*semicarbazone*, slender needles grouped in rosettes or large, transparent, apparently monoclinic prisms, m. p. 182°), which is not readily oxidised by nitric acid to *αα*-dipropyladipic acid; that the acid is actually formed, however, could be shown by converting the product of oxidation into its dimethyl ester (b. p. 158—160°/18 mm.), transforming the latter into methyl dipropyl*cyclo*pentanonecarboxylate, and further into 2:2-dipropyl*cyclo*pentanone (A., 1913, i, 485), the semicarbazone of which had m. p. 211°. 1-*Butyryl*-1-*propyl*cyclo*pentane* forms a colourless, volatile oil with an odour of peppermint, b. p. 115—117°/18 mm., D_4^{20} 0·8952, n_D^{20} 1·45544 (*semicarbazone*, m. p. 116°), the constitution of which follows from its smooth oxidation to 1-*propyl*cyclo*pentane*-1-*carboxylic acid*, colourless needles, m. p. 72°, b. p. 142°/18 mm.

The action of magnesium ethyl bromide on methyl *cyclo*hexan-1-ol-1-carboxylate (b. p. 96°/16 mm.) yielded a mixture of "as-*diethylpentamethylene glycol*" [1-*α-hydroxy-α-ethylpropyl*cyclo*hexan*-1-*ol*] and "*ethylpentamethylene glycol*" [1-*α-hydroxypropyl*cyclo*hexan*-1-*ol*], which could be incompletely separated, since the latter gradually crystallised in needles, m. p. 61—63°. The yield of pinacolin was unusually poor, and separation of the mixture of ketones was readily effected, since only the propionyl*cyclo*hexanone formed by loss of water from the residual "ethylpentamethylene

glycol"), colourless oil with the odour of amyl acetate, b. p. 196°/atmospheric pressure, 88—89°/19 mm., D_4^{20} 0·9105, n_D^{20} 1·45304 (*semicarbazone*, shining leaflets, m. p. 150—152°), proved capable of forming an *oxime*, four-sided plates, m. p. 70—72°. The portion which did not react with hydroxylamine consisted solely of 1-*propionyl*-1-*ethyl*cyclo*hexane*, colourless oil with the odour of peppermint, b. p. 109—111°/21 mm., D_4^{20} 0·9178, n_D^{20} 1·46292, the constitution of which follows from its unusually smooth oxidation to 1-*ethyl*cyclo*hexane*-1-*carboxylic acid*, m. p. 39—40°, b. p. 140°/15 mm.

It has been shown previously (A., 1913, i, 485) that hydroxybenzhydryl*cyclo*hexanol passes by loss of water into a so-called α-pinacolin, the corresponding oxide; it has now been found possible to convert the latter into the true β-pinacolin, 1-*benzoyl*-1-*phenyl*cyclo*hexane*, prisms, m. p. 73—74°, the constitution of which is deduced from its smooth fission by fusion with potassium hydroxide into phenyl*cyclo*hexane, m. p. 7°, b. p. 235—236°, and benzoic acid.

H. W.

Catalytic Preparation by the Dry Way of Ethyl Ether. A. Mailhe and F. de Godon (*Bull. Soc. chim.*, 1919, [iv], **25**, 565—568).—Aluminium oxide, as the catalyst, was prepared by heating commercial alum to 190—195°. Using a suitable amount of catalyst, disposed in four units, and heated in each case to 190—195°, a yield of ethyl ether equivalent to 71·3% of the theory was obtained when using 95% alcohol. The yield depends rather on the weight of the catalyst employed than on the surface exposed. It is also dependent on the concentration of the alcohol used.

W. G.

Action of Methyl Alcohol on Sulphuryl Chloride and on Methyl Chlorosulphonate. R. Levaillant and L. J. Simon (*Compt. rend.*, 1919, **169**, 854—857).—The action of methyl alcohol on sulphuryl chloride may be considered as occurring in two stages, namely,

(1) $SO_2Cl_2 + MeOH = OMe{\cdot}SO_2Cl + HCl$,

(2) $OMe{\cdot}SO_2Cl + MeOH = Me_2SO_4 + HCl$.

Another reaction, more important than that represented in (2), occurs, however, $OMe{\cdot}SO_2Cl + MeOH = MeHSO_4 + MeCl$. There are other secondary reactions, such as that of the hydrogen chloride and methyl alcohol with production of methyl chloride and water, which may affect the ultimate results of all the changes. The methyl hydrogen sulphate formed according to the third equation decomposes on distillation, giving methyl sulphate and sulphuric acid. By suitably modifying the conditions, a good yield of methyl chlorosulphonate may be obtained. [See, further, *J. Soc. Chem. Ind.*, 1919, 962A.]

W. G.

Preparation and Physical Properties of Dinitroglycol [Ethylene Dinitrate]. I. and II. Annibale Moreschi (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 393—397, 428—431).—Ethylene

dinitrate has been prepared according to the scheme: ethylene → ethylene dibromide → ethylene diacetate → ethylene glycol → ethylene dinitrate, the ethylene used being obtained in 96% yield by passing alcohol vapour over alumina heated at 350—360°, and the nitration of the glycol effected by means of a mixture of sulphuric and nitric acids. The specific gravities of ethylene dinitrate at $t°/4°$ vary rectilinearly with the temperature, and between 0° and 41·5° are given by the expression

$$1·4883[1-0·000775(t-15)];$$

the corresponding expression for glyceryl trinitrate between 0° and 55·5° is $1·5984[1-0·0008577(t-15)]$. The surface tension is also a linear function of the temperature: for ethylene nitrate, $4·76(1-0·0021t)$, and for glyceryl trinitrate, $5·18(1-0·003t)$. The viscosity of glyceryl trinitrate is far greater, and below 20° increases far more rapidly with fall of temperature, than that of ethylene dinitrate. The vapour tension of ethylene dinitrate at 20° is 0·3 mm.

The properties are given of various explosive products obtained by mixing ethylene dinitrate and glyceryl trinitrate with cellulose nitrate. T. H. P.

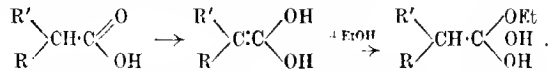
Reciprocal Influence of the Fatty Acids on the Solubility. P. Waentig and G. Pescheck (*Zeitsch. physikal. Chem.*, 1919, **93**, 529—569).—The solubility of a fatty acid in certain solvents is often very much increased by the presence of a second fatty acid. The increase is always reciprocal and often very considerable. For example, the solubility of palmitic acid in carbon tetrachloride is increased 250% by the presence of lauric acid. The increase in solubility decreases with increase of the disturbing acid and approaches a limiting value. An attempt is made to explain the increased solubility by the formation of readily soluble compounds of the two acids, but a direct proof could not be obtained, for molecular weight determinations, both by the ebullioscopic and cryoscopic methods, of one fatty acid in the presence of a second gave no difference in the boiling point or freezing point from that obtained with the pure solvent. But since the fatty acids are bimolecular in the solvents in which the increase of solubility is observed, this does not disprove the absence of compounds, for such compounds could well be formed without any change occurring in the number of molecules present, thus: $L_2+P_2=2LP$. If the view is correct, the formation of compounds, and also the increase in solubility, should not take place in those solvents in which the acids are unimolecular. It is found that in carbon tetrachloride, chloroform, benzene, toluene, and nitrobenzene solutions, in which the fatty acids are bimolecular, the increase in solubility occurs, but in ethyl alcohol, ethyl ether, ethyl acetate, and benzaldehyde solutions, in which the fatty acids are unimolecular, the increase in solubility is not observed. It is also found that the increase in solubility is not restricted to the fatty acids, but occurs also with aromatic acids, and in a much smaller degree with ketones and alcohols, so that it is suggested that the subsidiary valencies of the

carbonyl oxygen are responsible for the effect. A determination of the influence of temperature on the increase of solubility indicates that temperature has practically no effect on the increase. It is also shown that temperature has no influence on the association of the fatty acids in solution. The solubility of palmitic acid is influenced by the quantity of undissolved acid, and also to a very marked extent by traces of moisture. During the purification of palmitic acid, it was found that the solubility in a stated volume of a given solvent furnished a much better criterion of the purity of the acid than did the melting point. The density and vapour tension of liquid mixtures of fatty acids were determined, and it is shown that the values are not in keeping with the mixture law, from which it is deduced that compounds of the two acids are present in the fused mass. From the fusion curve of mixtures of palmitic and lauric acids, it is shown that an equimolecular compound of the two acids exists in the solid state. J. F. S.

Preparation of Chloromethyl Chloroformates. André Kling, D. Florentin, A. Lassieur, and R. Schmutz (*Compt. rend*, 1919, **169**, 1046—1047).—Carbonyl chloride condenses with methyl alcohol to give methyl chloroformate, which when acted on by chlorine in sunlight gives chloromethyl chloroformate, then dichloromethyl chloroformate, and finally the trichloromethyl ester. It is almost impossible to separate the first two esters by fractional distillation, but the dichloro- and trichloro-derivatives can be separated in this way. An alternative method is to chlorinate methyl formate in sunlight, but in this case some dichloromethyl formate is obtained. W. G.

Anomalies in the Formation of Esters from Acids and Alcohols. E. Preiswerk (*Helv. Chim. Acta*, 1919, **2**, 647—654).—Diethylmalonic acid cannot be esterified by alcohol and sulphuric acid or hydrogen chloride, the only ester which can be isolated being ethyl α-ethylpropionate in small quantity. Under similar conditions, ethyl malonate is formed in good yield from malonic acid.

A critical review of the literature on esterification leads the author to the conclusion that it is primarily an additive process. In general, however, there is but little tendency for the carbonyl portion of the carboxyl group to form additive compounds unless it is influenced by the presence of a neighbouring carbonyl group (as in oxalic or pyruvic acids) or by the tendency towards enolisation of a hydrogen atom in the α-position:



Esterification, according to this hypothesis, should occur most readily with acids containing a mobile α substituted hydrogen atom, and this appears to be the case when, for example, chloroacetic, cyanoacetic, and phenylacetic acids are compared with acetic

acid. As usually formulated, benzoic acid does not contain a hydrogen atom in the α-position, and yet it is readily esterified; the author seeks an explanation of the apparent anomaly in the oscillation hypothesis, which postulates the presence of the hydrogen atom in this position during the half-interval of time. The catalytic acceleration of esterification by mineral acids is attributed to the suppression of the ionisation of the organic acid, and consequent increase in the enolisation. H. W.

Some Ternary Systems containing Alkali Oxalates and Water. Albert Cherbury David Rivett and Edmund Arthur O'Connor (T., 1919, **115**, 1346—1354).

Preparation of Maleic Acid. John M. Weiss and Charles R. Downs (U.S. Pat. 1318632).—A mixture of benzene and benzoquinone in the vapour phase is oxidised by treatment under pressure with a gas containing oxygen at a temperature of 300—700° in the presence of vanadium oxide. The maleic acid produced is separated, and the residual, unchanged benzene and benzoquinone are again subjected to the same treatment.
G. F. M.

Slow, Partial Change of an Aqueous Solution of Maleic Acid into Fumaric Acid at the Ordinary Temperature and in the Absence of Light. Anton Kailan (*Zeitsch. physikal. Chem.*, 1919, **93**, 613—616).—From electro conductivity measurements with a solution of maleic acid which had been kept in the dark for five years, it is shown that about 4% of the acid had become changed into fumaric acid. J. F. S.

Various Bismuth Compounds. L. Vanino and F. Mussgnug (*Arch. Pharm.*, 1919, **257**, 267—269).—The following bismuth salts have been prepared with the help of bismuth–mannitol solution, obtained by grinding together crystalline bismuth nitrate (1 mol.) and mannitol (1 mol.) and treating the mass with water.

Bismuth anhydromethylenecitrate, $Bi_2(C_7H_6O_7)_3.6H_2O$, prepared from the corresponding sodium salt ("citarine") and bismuth–mannitol, forms an odourless, white, granular powder, and is reduced to metallic bismuth when heated with alkali hydroxide.

Bismuth diethylmalonate, $Bi_2(C_7H_{10}O_4)_3$, is obtained as a voluminous, white precipitate from the sodium salt and bismuth–mannitol solution.

Bismuth mandelate, $Bi(C_8H_7O_3)_3$, prepared from mandelic acid and bismuth–mannitol solution, forms a white, indistinctly crystalline precipitate, m. p. 210—215° (decomp.).

Bismuth vanillate, $Bi(C_8H_7O_4)_3.2H_2O$, obtained from the sodium salt and bismuth–mannitol solution, forms yellowish-white, nodular crystals with no sharp melting point.

Bismuth cinnamate, $Bi(C_9H_7O_2)_3.3H_2O$, forms nodular crystals with an indistinct melting point.

Bismuth acetate may be prepared in 95% yield by heating bismuth

oxide or hydroxide in a reflux apparatus with acetic anhydride, its formation being accelerated by the presence of a little glacial acetic acid. T. H. P.

Preparation of Formaldehyde from Formates. H. and S. (*Caoutchouc et Guttapercha*, 1919, **16**, 9803; from *Chem. Zentr.*, 1919, iv, 412).—Formaldehyde is produced when metallic formates are heated, the necessary temperature increasing with increase in the basic properties of the metal. The optimum temperatures are as follows: Cu, 170°; Pb, 195—200°; Ni, 210°; Zn, 240°; Fe, 245°; Mn, 295°; Ba, 325°; Ca, 335°; Mg, 340°; Sr, 355°; Na, 355°; K, 375°. A large portion of the formaldehyde is immediately transformed into methyl alcohol and formic acid. Methyl alcohol and formaldehyde are produced when formic acid is passed at the high temperature over zinc oxide or thorium oxide. H. W.

Diastase-like Properties of Formaldehyde. Action of Formaldehyde on Starch. Harry Maggi (*Fermentforsch.*, 1919, **2**, 304—447; from *Chem. Zentr.*, 1919, iii, 635).—The main results obtained in the investigations have already been reported by Woker. The apparent degradation of starch appears to proceed most readily in faintly acid solution. Experiments are now recorded on the action of mixtures of formaldehyde or saliva with glycogen solution and iodine and on the precipitation of starch or glycogen by formaldehyde. The latter phenomenon is also observed with formic or other acids. A method of estimating diastase, based on the alteration in shade in the mixtures described above, could not be worked out in consequence of this action. H. W.

The Diastase-like Properties of Formaldehyde. G. Woker and H. Maggi (*Ber.*, 1919, **52**, [*B*], 1594—1604).—The authors reiterate their arguments in favour of the view that formaldehyde acts on starch in a certain measure like diastase, and reply to recent criticisms (A., 1919, i, 253, 311, 312). They hold the view that under the prolonged influence of formaldehyde the primary hydrolytic products are rebuilt into non-hydrolysable and non-reducing substances, such as the so-called "reversion dextrin," and in this way they meet most of the criticism, for the authors, in their desire to give the hydrolysis every assistance of time and temperature, did just the reverse by generally keeping the mixtures of starch and formaldehyde too long. A similar rebuilding of hydrolytic products is known to occur when egg albumen is digested with papain (see Abderhalden's book). J. C. W.

The Stabilisation of Acraldehyde. III. Preparation of Acraldehyde. Charles Moureu and Adolphe Lepape (*Compt. rend.*, 1919, **169**, 885—889).—For the preparation of acraldehyde from glycerol the authors recommend the use of a mixture of 5 parts of potassium hydrogen sulphate with 1 part of potassium sulphate as a dehydrating agent. Using such a mixture, to which is added one-quarter of its weight of glycerol, the heating being

carefully controlled and the glycerol replaced as exhausted, they obtained a yield of pure acraldehyde equivalent to 67·5% of the theoretical yield. [See, further, *J. Soc. Chem. Ind.*, 1920, 42A.]

W. G.

γ-Hydroxyaldehydes. II. BURCKHARDT HELFERICH (*Ber.*, 1919, 52, [*B*], 1800—1812. Compare A., 1919, i, 386).—In the former paper it was shown that γ-hydroxyvaleraldehyde behaves like a furan derivative, and yields an acetate and a methyl compound of the same type. Starting with methylheptenol, this has now been acetylated and methylated, the derivatives ozonised in glacial acetic acid, and then treated with zinc dust, giving the acetate and methyl ether of the normal form of γ-hydroxyvaleraldehyde. The isomerides differ in molecular refraction and chemical properties in the expected manner. Apparently, the free γ-hydroxyvaleraldehyde, or rather 2-hydroxy-5-methyltetrahydrofuran, is desmotropic with the true aldehyde form, thus:

$$O\!<\!\begin{matrix}CH(OH)\cdot CH_2\\ |\\ CHMe-CH_2\end{matrix} \rightleftharpoons OH\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHO,$$

which may be demonstrated as follows: by adding equal quantities of Schiff's reagent or ammoniacal silver oxide to equivalent solutions of "γ-hydroxyvaleraldehyde" (1%), γ-methoxyvaleraldehyde and acetaldehyde (0·44%), the characteristic reactions are complete in a few seconds with the true aldehydes, but develop gradually with the furan derivative. Similar phenomena are exhibited by γ-hydroxyhexaldehyde.

Acetylmethylheptenol [*αε-dimethyl-Δ-hexenyl acetate*], $CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot OAc$, from methylheptenol and acetic anhydride, has b. p. 78—78·5°/9 mm., $D_4^{15\cdot5}$ 0·8928, $n_D^{17\cdot5}$ 1·4328, and *methylheptenol methyl ether* [*β-methoxy-ζ-methyl-Δ-heptene*], from methylheptenol, sodium, and methyl iodide, has b. p. 50—50·5°/9 mm., 163·5°/752 mm. (corr.), D_4^{15} 0·8103, n_D^{15} 1·4281. *γ-Acetoxyvaleraldehyde* has b. p. 88—91°/12 mm., D_4^{15} 1·011, n_D^{15} 1·4226, and is very sparingly soluble in water. *γ-Methoxyvaleraldehyde*, $OMe\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHO$, is a limpid, mobile liquid, soluble in water (1 in 5), b. p. 43—44°/10 mm., D_4^{18} 0·9161, n_D^{18} 1·4134.

Whereas the furan derivative is merely converted into its methyl ether, 2-methoxy-5-methyltetrahydrofuran, under the influence of methyl-alcoholic hydrogen chloride, the true γ-methoxyvaleraldehyde, like aldol (prepared by Grignard's method, A., 1907, i, 287), gives a dimethylacetal. *αaδ-Trimethoxypentane*, from methoxyvaleraldehyde, is a very soluble liquid with a burning taste, b. p. 99°/12 mm., D_4^{18} 0·9197, n_D^{18} 1·4119, and *αα-dimethoxybutan-γ-ol*, from aldol, has b. p. 71—76°/9 mm., D_4^{18} 0·9894, n_D^{18} 1·4200.

Just as aldol may be converted into pentan-βδ-diol by means of magnesium methyl iodide, so γ-methoxyvaleraldehyde yields *ε-methoxyhexan-β-ol*, $OH\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHMe\cdot OMe$, b. p. 79—80°/9 mm., D_4^{18} 0·9048, n_D^{18} 1·4263. Similarly, if the free

"γ-hydroxyvaleraldehyde" were a true aldehyde it would form the known hexane-βε-diol, but whilst it reacts to form methane, the intermediate magnesium compound regenerates the original substance and complex products on decomposition with dilute sulphuric acid.

Δ$^{\gamma}$-Pentenoyl chloride is slowly added to well-chilled zinc ethyl and the product is decomposed by ice, giving *ethyl* Δ$^{\gamma}$-*butenyl ketone*, CH_2:$CH{\cdot}CH_2{\cdot}CH_2{\cdot}COEt$, b. p. 46—47°/12 mm., $D_4^{18\cdot3}$ 0·8487, $n_D^{18\cdot3}$ 1·4254, an unpleasant-smelling liquid, which forms a *semicarbazone*, thin, rhombic plates, m. p. 82—83° (corr.), and is reduced by sodium and alcohol to Δ$^{\epsilon}$-*hepten-ε-ol*, b. p. 60—61·5°/11 mm., D_4^{18} 0·8447, n_D^{18} 1·4369. This is ozonised as above, and thus converted into γ-*hydroxyhexaldehyde* [or, rather, the desmotrope, 5-*hydroxy*-2-*ethyltetrahydrofuran*], a fairly mobile, limpid liquid, b. p. 77—80°/11 mm., D_4^{18} 1·004, n_D^{18} 1·4398, which condenses with methyl alcohol to form the half-acetal, that is, 5-*methoxy*-2-*ethyltetrahydrofuran*, b. p. 139—145°/760 mm. (corr.), D_4^{18} 0·9225, n_D^{18} 1·4164, a mobile oil with odour reminiscent of peppermint. J. C. W.

Manufacture of Acetone and Carbon Dioxide. Société Anonyme des Acieries & Forges de Firminy (Brit. Pat., 134144).—Acetic acid of 90—100% strength is catalysed over manganese peroxides prepared either by precipitation or by crushing and screening natural pyrolusite, pieces of a diameter of 5—7 mm. being employed. Catalysis occurs without appreciable subsidiary reaction between wide limits of temperature, for instance, 350—450°. The catalyst is packed in a cylinder and heated either externally or, preferably, by mixing with 1—1½ volumes of crushed coke similarly screened, and passing an electric current through the mixture by means of two iron or aluminium electrodes. The acetone produced is separated from the carbon dioxide by condensation, and scrubbing in water-sprinkling towers. The catalyst is much more stable than Sabatier's manganous oxide, and when the activity does decline, it is only necessary to heat it in a current of air to revivify it.

G. F. M.

The Production of Methyl Ethyl Ketone from *n*-Butyl Alcohol. Albert Theodore King (T., 1919, **115**, 1404—1410).

Physical Properties of Mannitol and its Aqueous Solutions. Joseph M. Braham (*J. Amer. Chem. Soc.*, 1919, **41**, 1707—1718).—The melting point, the specific rotation in aqueous solution, and the freezing-point solubility diagram of pure mannitol up to 103° have been determined. The most trustworthy values of the density, specific heat, and heat of combustion are indicated from a discussion of the various values occurring in the literature. The following physical constants are recorded: melting point, 166·05°; specific rotation, $[\alpha]_F^{25} = -0{\cdot}244 \pm 0{\cdot}002°$, and $[\alpha]_E^{25}$ calculated $= -0{\cdot}208 \pm 0{\cdot}002°$; D 1·487 (room temperature), specific heat C (28—100°) = 0·3271 cal./deg., and C (14—26°) = 0·315 cal./deg.;

heat of combustion, 4·00 cal./gram. Pure mannitol may be obtained from the commercial product by two crystallisations from aqueous alcohol. J. F. S.

Conversion of the Simple Sugars into their Enolic and Ethylene Oxide Forms. EDWARD FRANKLAND ARMSTRONG and THOMAS PERCY HILDITCH (T., 1919, **115**, 1410—1428).

Action of the Carbonates of the Alkaline Earths on Dextrose. HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1919, **97**, 97—113).—When a solution of dextrose is boiled with calcium carbonate, it becomes brown, and gradually loses its dextro-rotation, which after prolonged boiling is entirely eliminated; the sugar may even become lævorotatory. The reducing power of the dextrose is also diminished, but to a much smaller extent. Distilled water previously shaken with calcium carbonate produces the same change, but the reduction in the rotation becomes constant after some time because the dissolved carbonate is neutralised by the acid formed in the reaction. It is concluded that the dextrose is changed into lævulose, and eventually into other lævorotatory or weakly dextrorotatory sugars. S. S. Z.

Synthesis of Disaccharides with Two Sulphur or Selenium Atoms. FRITZ WREDE (*Ber.*, 1919, **52**, [*B*], 1756—1761).—Acetobromoglucose reacts with potassium disulphide in alcohol to form a disulphide of the type R_2S_2, mixed with various by-products. Some of these are partly de-acetylated compounds, but they may be re-acetylated by means of acetic anhydride and the complication thus removed. To a certain extent the potassium disulphide reacts as a mixture of sulphur and monosulphide, the latter forming the octa-acetate of thio*iso*trehalose, R_2S (A., 1917, i, 540), and apparently also according to the scheme $R_2S_2 + 2K_2S = 2R{\cdot}SK + K_2S_2$. The mono- and di-sulphides can be separated by fractional crystallisation, and the acetyl groups removed by means of methyl-alcoholic ammonia. Similar selenium compounds may also be obtained.

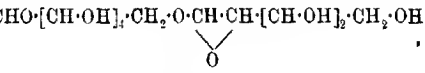
Octa-acetyldithiodiglucose, $C_{28}H_{38}O_{18}S_2$, crystallises in stout crusts from benzene or long needles from methyl alcohol; m. p. 139°, $[\alpha]_D^{18}$ −177·7° in nitrobenzene. *Dithiodiglucose*, $C_{12}H_{22}O_{10}S_2$, is a hygroscopic, white powder, $[\alpha]_D^{18}$ −144·4° in water, which tastes sweet, and forms metallic salts, for example, the *potassium* salt, $C_{12}H_{20}O_{10}S_2K_2.2H_2O$. *Octa-acetyldiselenodiglucose* has m. p. 133°, $[\alpha]_D^{18}$ −133·8° in chloroform, and *diselenodiglucose* is a pale yellow powder, $[\alpha]_D^{18}$ −93·98° in water, which forms a *potassium* salt, $C_{12}H_{20}O_{10}Se_2K_2.2H_2O$. J. C. W.

Density of Pure Sucrose and the Contraction in Volume of its Aqueous Solutions. D. SIDERSKY (*Bull. Assoc. Chim. Sucr. Dist.*, 1919, **37**, 73—77).—From the tables of specific gravities of aqueous sucrose solutions compiled by Plato in 1900 (and adopted by the German *Normal Eichungs-Kommission*), the author has calculated the solution density of sugar at different concentrations, the solvent being assumed to occupy the same volume as in the pure

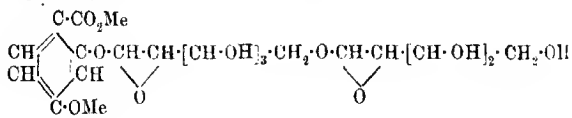
state. For concentrations ranging from 5 to 90 grams of sucrose per 100 c.c. absolute, at 15°, the solution densities range almost linearly from 1·629 to 1·591, thus approaching the density of solid sugar (1·588) as the limit of solubility is reached. The contraction which accompanies the formation of sucrose solutions increases with the concentration of sugar to a maximum value of 0·47% of the total volume for solutions containing 45—55 grams per 100 c.c., beyond which concentration it declines again, and amounts to only 0·11% for solutions containing 90 grams per 100 c.c. J. H. L.

Characteristics and Composition of Primeverose. A. Goris and Ch. Vischniac (*Compt. rend.*, 1919, **169**, 871—873).—A further study of the sugar primeverose, obtained from the two glucosides primeverin and primulaverin isolated from *Primula officinalis*, Jacq (compare A., 1913, i, 576). This sugar crystallises in the anhydrous state and has m. p. 209—210°. It shows mutarotation, initial $[\alpha]_D$ +22·70°, final $[\alpha]_D$ −3·43°. It reduces Fehling's solution, gives an *osazone*, m. p. 224—225°, and on hydrolysis gives one molecule of dextrose and one molecule of xylose. W. G.

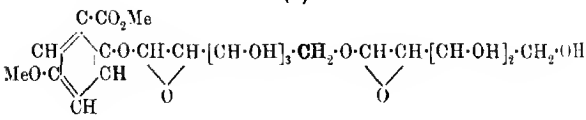
Constitution of Primeverose, Primeverin, and Primulaverin. A. Goris and Ch. Vischniac (*Compt. rend.*, 1919, **169**, 975—977).—It has previously been shown (preceding abstract) that primeverose is a biose formed by the combination of a molecule of dextrose and a molecule of xylose, and that it has a free aldehyde group. It has now been shown by controlled oxidation of the sugar and subsequent hydrolysis of the *calcium primeverobionate* formed that the free aldehyde group is in the dextrose residue. The constitution of primeverose is, therefore, given as



Similarly, it has been shown that primeverin and primulaverin give, on hydrolysis, primeverose and the methyl esters of β-methoxyresorcylic acid and *m*-methoxysalicylic acid respectively. These two compounds have, therefore, the constitutions shown in formulæ I and II respectively:



(I.)



(II.)

W. G.

Systematic Ageing Experiments with Solutions of Various Kinds of Starch under Exact Time Conditions. Time Law of the Ageing of Starch Solutions. HERMANN SALLINGER (*Kolloid Zeitsch.*, 1919, **25**, 111—115).—Experiments on the ageing of starch solutions have been carried out with soluble potato starch, soluble wheat starch, soluble barley starch, and with amylodextrin from potato starch. The solutions were made up in water, and at stated intervals 50 c.c. of the solution were treated with 0·5 c.c. of human saliva (ptyalin) and kept for twenty-three hours at the ordinary temperature; the precipitated starch gel was filtered and dried at 110° until of constant weight. If G is the weight of gel and t the time of ageing in hours it is found that the relationship between $\log G$ and $\log t$ is represented by a straight line, and that numerically $G=gt^a$, where g and a are constants. These values have been determined for the starch varieties named above, and it is shown that they are characteristic of the variety. The following values are recorded: potato starch I., $g=4·06$, $a=0·445$; potato starch II, $g=3·00$, $a=0·455$; wheat starch, $g=5·37$, $a=0·165$; barley starch, $g=11·17$, $a=0·214$; amylodextrin, $g=3·51$, $a=0·521$. The starch solutions were aged at 7°. J. F. S.

Studies in Fermentation. HERMANN SALLINGER (*Fermentforsch.*, 2, 449—457; from *Chem. Zentr.*, 1919, iii, 635).—A reply to Biedermann (A., 1917, i, 62). The author sets out in detail the reasons which lead him to consider the application of extremely dilute solutions, as recommended by Biedermann, unsuitable. Experiments with sterilised starch solution failed to confirm the diastatic action of saliva ash or the autolysis of starch. H. W.

Studies in Fermentation. IV. Autolysis of Starch. W. BIEDERMANN (*Fermentforsch.*, **2**, 458—472; from *Chem. Zentr.*, 1919, iii, 635).—The autolysis of starch might possibly be due to traces of ferments retained by the crude material. The former experiments (A., 1917, i, 62; 1919, i, 107) have therefore been repeated with preparations of amylose which had been purified by boiling and treatment with hydrochloric acid. The experimental procedure is very fully described. The author has endeavoured to disprove the possible criticism that the results are due to bacterial action by control experiments in which a culture of bacteria which readily cause the fission of starch was added to the amylose solution; the achromic point was reached very much more slowly than in the presence of saliva ash or sodium chloride. The activity of the salts is not due to their power of directly causing the fission of starch, but is to be ascribed to their action in facilitating the formation of the ferment; when once this is attained in a sufficient degree, autolysis proceeds unaltered in a solution which has been freed from salts by dialysis. Preparations which already contain fission products of starch are less readily affected, and require much longer periods than pure amylose preparations. H. W.

Cellulose and Cellulose Nitrate. Absorbent Power for Gases and Constitution. B. Oddo (*Gazzetta*, 1919, **49**, ii, 127—139).—Cellulose is able to fix acid gases in definite proportion, one molecule of dry hydrogen chloride being taken up per one quadrupled molecule (C_{24}) of cellulose. Of the other gases examined only ammonia is absorbed in approximately the above proportion. In all cases the volumes of different gases absorbed increase with their solubility in water and diminish in the following order: NH_3, HCl, SO_2, H_2S, N_2O, CO_2, C_2H_2, CO, O, N, CH_4, H. Charcoal which has absorbed a certain gas loses part of this when immersed in a second gas, the latter being absorbed to some extent without chemical action taking place. A similar phenomenon sometimes occurs with cellulose, but whereas carbon dioxide displaces ammonia and sulphur dioxide, it does not displace hydrogen chloride. The latter appears, therefore, to enter into true chemical combination, either being added to the ethereal oxygen with formation of an oxonium compound, $:O<^{H}_{Cl}$, or giving a grouping similar to that obtained with aldehydic compounds, $\cdot CH:O + HCl = \cdot CHCl\cdot OH$.

By deca- and endeca-nitrated celluloses dry hydrogen chloride is at first absorbed with great rapidity, but after a time red vapours are emitted and, even after being kept in an evacuated space, the product contains ionic chlorine and small proportions of nitrogen. The volume of sulphur dioxide absorbed by nitrated cellulose (13·32% N) is about five times that absorbed by an equal weight of cellulose. T. H. P.

Nitroacetylcellulose [Cellulose Nitrate Acetate]. B. Oddo (*Gazzetta*, 1919, **49**, ii, 140—145).—The author has prepared a cellulose nitrate acetate by the action of boiling acetic anhydride on a collodion cotton (11·68% N), probably consisting principally of octanitrated cellulose, $C_{24}H_{28}O_8(O\cdot NO_2)_8(OH)_4$. The percentage of nitrogen and the number of acetyl groups in the product obtained indicate it to be a tetra-acetate octanitrate of cellulose, but cryoscopic determination of the molecular weight in acetic acid at low concentrations (0·42—2·1%) gives results corresponding closely with the formula $C_6H_7O_2(O\cdot NO_2)_2\cdot OAc$; as the concentration of the solution is increased, the molecular weight also increases, and reaches the quadruple value only when the concentration is about 21%. When purified, the substance is quite white, and begins to contract at 175°, whilst at 184·5° it decomposes with evolution of gas bubbles. It does not reduce Fehling's solution, but, like cellulose nitrate, gives a yellow coloration when moistened with dilute sulphuric acid and treated with a solution of iodine in potassium iodide. In the air it burns rapidly with an orange-yellow flame, leaving a small, partly carbonised residue. It dissolves in the hot in dilute, and in the cold in concentrated, alkali hydroxide solution; it is soluble in concentrated sulphuric acid, addition of mercury to the solution resulting in the liberation of nitric oxide. T. H. P.

The Use of Thallium in Organic Chemistry. KARL FREUDENBERG and GERTRUD UTHEMANN (*Ber.*, 1919, **52**, [*B*], 1509—1513).—Thallium hydroxide or carbonate has proved useful in the isolation of acids of the gallic acid series (A., 1919, i, 413), and it is now shown that uric acid, phthalimide, and lævulose give well-defined *thallium* salts. Glycine may also be prepared from the hydrochloride of its ester by boiling this with thallium carbonate and water, filtering the precipitate of thallium chloride, saturating with hydrogen sulphide, and filtering again.

Solutions of convenient thallium compounds are prepared as follows. Thallium turnings are suspended over alcohol in an atmosphere of oxygen, when oily thallium "ethoxide" is produced, and also a 5% solution of this in alcohol. The oil is really a mixture or compound of ethoxide and hydroxide in slightly varying proportions, formed according to the equation $2Tl + O + EtOH = TlOEt + TlOH$. It is freely soluble in pure ether. The hydroxide is obtained by mixing the oil with water and evaporating the alcohol under reduced pressure. The saturated aqueous solutions are about $2N$ (400 grams per litre). A concentrated solution of a hydrogen carbonate (200 grams Tl per litre) is produced by saturating a suspension of the hydroxide with carbon dioxide.

J. C. W.

Alkylamino-chromium Compounds. IV. Compounds with Methyl-, *n*-Butyl-, and *iso*-Amyl-amines. HJ. MANDAL (*Ber.*, 1919, **52**, [*B*], 1489—1500. Compare A., 1919, i, 257).—The following *chloropentamethylaminochromic* salts have been prepared: chloride, $[CrCl(NH_2Me)_5]Cl_2$, by the action of methylamine on anhydrous chromic chloride at $-10°$ (Lang and Carson, A., 1904, i, 800); *bromide*, glistening, violet prisms, and *iodide*, by double decomposition of the chloride with the potassium haloid; *mercurichloride*, $XCl_2,3HgCl_2$, pale red, *mercuribromide*,

$$XBr_2,HgBr_2,$$

reddish-violet, stellate groups, and red *mercuri-iodide*, XI_2,HgI_2, by the addition of the potassium mercuri-haloids to the above haloids; *platinichloride*, $XPtCl_6$, microcrystalline, chamois-coloured powder, and *bismuthichloride*, $XCl_2,BiCl_3$, pale violet, by the addition of the metallic chloride to hydrochloric acid solutions of the above chloride; yellow *pentasulphide*, XS_5, by the addition of yellow ammonium sulphide to the chloride.

Chloropenta-n-*butylaminochromic chloride*.

$$[CrCl(NH_2{\cdot}C_4H_9)_5]Cl_2.$$

and *chloropentaisoamylaminochromic chloride*.

$$[CrCl(NH_2{\cdot}C_5H_{11})_5]Cl_2,$$

are obtained by gently boiling the amines with chromic chloride. They are successively deeper violet in colour than the lower isomerides, but they are decomposed by water and are not easy to purify.

Dichlorotetra-n-*propylaminochromic chloride*,

$$[CrCl_2(NH_2Pr^n)_4]Cl.$$

is formed as a by-product in the preparation of the pentapropylamine compound (*loc. cit.*) if the mixture becomes too hot. It crystallises in very dark green prisms, and the *nitrate* is greyish-green. *Dichlorotetra-n-butylaminochromic chloride*, small, green prisms, and *dichlorotetraisoamylaminochromic chloride*, a greyish-green powder, are prepared by the addition of concentrated hydrochloric acid to alcoholic solutions of the penta-alkylamino-compounds. J. C. W.

Manufacture of Salts or Compounds of Choline and of its Higher Homologues. Vereinigte Chemische Werke (Brit. Pat., 8031 of 1914).—Solutions of the compounds or salts of choline with such acids as boric, salicylic, o-, *m*-, or *p*-iodobenzoic, *p*-aminophenylarsinic, 3-iodo-4-aminophenylarsinic, or formic acid, whilst having a similar action to choline itself on cell tissues when injected into the blood, have the advantage of increased stability and consequent non-formation of poisonous decomposition products. The action of these compounds is therefore quite different from that of salts of choline with mineral acids, which have a negligibly small action on living cells. [See, further, *J. Soc. Chem. Ind.*, 1920, 43A.] G. F. M.

The Decomposition of Carbamide in the Presence of Nitric Acid. Tudor Williams Price (T., 1919, **115**, 1354—1360).

Compounds of Complex Cyanides with Mercuric Cyanide. D. Strömholm (*Zeitsch. anorg. Chem.*, 1919, **108**, 111—112).—When a warm, concentrated aqueous solution of equivalent quantities of potassium platinocyanide and mercuric cyanide is allowed to cool, white, crystalline needles of a double salt having the composition $K_2Pt(CN)_4.Hg(CN)_2.2H_2O$ separate. A similar compound of potassium nickel cyanide and mercuric cyanide was prepared. Mercuric cyanide does not form compounds with potassium ferricyanide, cobalticyanide, chromicyanide, or with the compound $K_4Mo(CN)_8$. E. H. R.

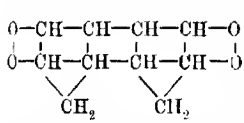
The Constitution of the Nitroprussides. I. Conductivity and Cryoscopic Measurements. George Joseph Burrows and Eustace Ebenezer Turner (T., 1919, **115**, 1429—1435).

Action of Acetylene on Arsenic Trichloride. Orville A. Dafert (*Monatsh.*, 1919, **40**, 313—323).—Acetylene does not react to any considerable extent with arsenic chloride at the ordinary temperature or at the boiling point of the latter; in the presence of anhydrous aluminium chloride at the ordinary temperature, however, *diacetylene arsenic trichloride*, $AsCl_3.2C_2H_2$, is readily formed as a heavy, yellow oil, D^{15} 1·6910, b. p. 250°. Its vapours are strongly irritating, but not markedly poisonous, although exhibiting strong bactericidal power. When compared with the corresponding antimony and aluminium compounds, the arsenic

derivative exhibits a remarkable stability, since it can be distilled and is not decomposed by water. When heated with potassium hydroxide solution, it evolves acetylene. At a higher temperature, arsenic trichloride and acetylene in the presence of aluminium chloride yield a black, organo-arsenic *compound* of high molecular weight which is very stable towards reagents, but sensitive to light, and in its properties resembles the aluminium derivative prepared by Baud in a similar manner; it contains 7·70% As, 69·25% C, 5·18% H, and 7·87% O. [Total, 90% only.] H. W.

Organo-metallic Compounds. II. The Action of Carbon Monoxide on Sodium Alkyls. Hans Heinrich Schlubach (*Ber.*, 1919, **52**, [*B*], 1910—1914).—Carbon monoxide is readily absorbed by mixtures of sodium and mercury diethyl or mercury diphenyl in light petroleum or benzene, that is, by the organo-sodium compounds (compare Schlenk, A., 1917, i, 255). In the case of sodium ethyl the products are diethyl ketone, triethylcarbinol, and propionic acid, whilst the smoother reaction in the case of sodium phenyl gives rise to benzophenone (30%), triphenylcarbinol (25%), and benzoic acid (16%), the yields being calculated on the weight of mercury diphenyl used. J. C. W.

***cyclo*Pentadiene and its Dimeride.** Hans Stobbe and Fritz Dünnhaupt (*Ber.*, 1919, **52**, [*B*], 1436—1442).—From the result of refraction measurements made a few years ago, Stobbe concluded that *cyclo*pentadiene changes almost completely into a dimeride within thirty days at 20° (A., 1912, i, 842). The nature of the atmosphere above the oil, whether air or carbon dioxide, seemed to have no great influence on the rate at which the refractive index rose. Inasmuch as the hydrocarbon, and especially its dimeride, spontaneously absorb oxygen, it remained to be proved whether the polymerisation is accompanied by autoxidation. It is actually found that the end-product of the polymerisation when the oil is freely exposed to oxygen is not the dimeride, but its di-peroxide, probably represented by the annexed formula. In the absence of oxygen, the end-product has a slightly greater refractive index. The rate at which polymerisation proceeds is distinctly, but only very slightly, greater in the light than in the dark. J. C. W.



The Benzene [Formula] Problem. II. A. von Weinberg (*Ber.*, 1919, **52**, [*B*], 1501—1508).—See this vol., ii, 14.

Catalytic Oxidation of Benzene. John M. Weiss and Charles R. Downs (U.S. Pat. 1318633).—Benzene is oxidised to compounds containing hydrogen, oxygen, and less than six carbon atoms by the action of a gas containing oxygen at a temperature of 300—500° in the presence of a catalyst. G. F. M.

Oxidation of Side-chains with Potassium Permanganate. Lucius A. Bigelow (*J. Amer. Chem. Soc.*, 1919, **41**, 1559—1581). —The action of potassium permanganate in alkaline solution on three nitrotoluenes has been investigated. The experiments were generally performed by gradually adding the solid permanganate to a boiling suspension of the nitrotoluene in aqueous sodium hydroxide solution; in the case of *p*-nitrotoluene, oxidation was also effected at lower temperatures, but the yields were considerably decreased and the duration of the experiments greatly prolonged.

Changes in the conditions of oxidation, in general, merely cause a different proportion of the nitrotoluene to be attacked by the oxidising action, the ratio of nitrobenzoic acid produced to unchanged nitrotoluene remaining essentially constant. The conclusions are therefore drawn that the quantity of nitrotoluene or nitrobenzoic acid entirely destroyed by the oxidising agent is practically constant and almost independent of the oxidation procedure, and that at least two entirely independent actions take place simultaneously in the oxidising mixture, namely, the oxidation of the organic compound and the decomposition of the permanganate into manganese oxides and free oxygen. It is somewhat curious to note, however, that solutions containing alkali and permanganate, in the proportions most frequently used in this work, do not decrease in oxidising power when boiled for protracted periods in the absence of organic matter.

Increase in the concentration of the alkali in the oxidising mixture up to a certain point favours the oxidation of *o*-nitrotoluene, beyond which point a further increase produces essentially no effect, all other conditions being kept constant. By this increase in alkaline concentration, the oxidation of the meta-isomeride is hindered, such oxidation being most effective in an essentially neutral medium; with *p*-nitrotoluene, oxidation is favoured up to a certain point, beyond which the quality of the product becomes very poor. Possibly, acceleration of the oxidation of the ortho- and para-isomerides by alkali is due to their conversion into a quinonoid form, which is impossible with the meta-derivative.

Increasing dilution of the reaction mixture favours the oxidation of all the nitrotoluenes, probably owing to retardation of the decomposition of the permanganate into manganese oxides and oxygen.

In all circumstances, *p*-nitrotoluene is oxidised most readily, the ortho-compound next, and the meta-isomeride least readily.

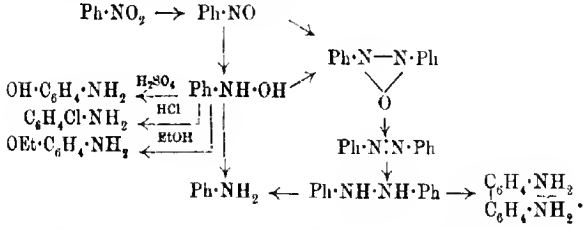
Catalytic influences have been studied by carrying out the oxidations of *o*- and *p*-nitrotoluenes in iron, copper, and enamel-lined vessels respectively. In both cases nearly the same results were obtained in the copper and enamel-lined containers, but distinctly lower yields and products of poorer quality in the iron vessel both with and without alkali. The addition of salts of calcium and magnesium to the reaction mixture in the oxidation of *p*-nitrotoluene in neutral solution produced no noticeable effect, and a similar result was obtained after addition of pyridine to a similar oxidation in alkaline solution, although it acts as a powerful negative catalyst in certain permanganate reactions.

A practical method for the preparation of *m*-nitrotoluene has been elaborated, consisting in the nitration of aceto-*p*-toluidide to *m*-nitroaceto-*p*-toluidide, hydrolysis of the acetyl group, and elimination of the amino-group; the details are fully discussed in the original paper. H. W.

Production of Benzyl Chloride and Benzylidene Chloride and of certain Homologues and Substitution Products of these Compounds. Levinstein, Ltd., Herbert Levinstein, and Walter Bader (Brit. Pat. 134250).—Substitution products containing chlorine in the side-chain are obtained by treating hydrocarbons at temperatures below 0° with hypochlorous acid in aqueous solution. For example, toluene (3 mols.) is emulsified with a hypochlorite solution containing 1 mol. of active chlorine, and after cooling to −5° dilute sulphuric or other acid (1 equivalent) is gradually added. The product, containing unchanged toluene, 60—70% of the theoretical quantity of benzyl chloride, and small quantities of benzylidene chloride and higher chlorinated products, is purified by fractional distillation. A second atom of chlorine may be similarly introduced, it occupying preferably a position in the methyl group already substituted if more than one are present. Monochlorotoluenes behave similarly, but the higher chlorinated toluenes, nitro-substitution products, sulphonyl chlorides, and cresol esters do not give side-chain substitution products under these conditions. Sulphonic acids are substituted in the nucleus.

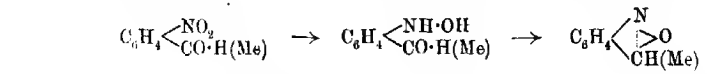
G. F. M.

Determination of the Course of the Reaction in the Catalytic Reduction of Nitrobenzene. F. F. Nord (*Ber.*, 1919, **52**, [*B*], 1705—1712).—In the reduction of nitrobenzene by chemical or electrical means, it is evident that phenylhydroxylamine plays an important part, as the following scheme indicates:



It appeared to be of interest, therefore, to determine whether it is formed during the catalytic reduction of nitrobenzene by means of colloidal platinum protected by gum arabic, but this mode of reduction offers very little scope for controlling the rate of the reaction and isolating any intermediate products, compared with the electrolytic method. To surmount this difficulty, the reduction of *o*-nitrobenzaldehyde and *o*-nitroacetophenone was tested, for the aldehyde or ketone group in the ortho-position is capable of form-

ing anthranils through condensation with the hydroxylamine group, thus:



(compare Bamberger and others, A., 1904, i, 93; 1909, i, 509, 511). By stopping the reaction after two molecular proportions of hydrogen were absorbed, the anthranils could, indeed, be isolated.

The rate at which nitrobenzene is reduced to aniline is practically constant, and so it is during the reduction of *o*-nitroacetophenone to *o*-aminoacetophenone, the yields being quantitative. In the case of *o*-nitrobenzaldehyde, however, there is a very considerable lag after the anthranil stage is reached. The absorption of the third molecular proportion of hydrogen takes about twelve times as long and the product contains only a small quantity of *o*-aminobenzaldehyde. The chief product is Friedländer and Göhring's pale yellow condensation product of *o*-aminobenzaldehyde, m. p. 183—186° (A., 1884, 1019). J. C. W.

The Nitrotoluenes. I. Binary Systems of a Nitrotoluene and s-Trinitro-*m*-xylene. James M. Bell and James P. Sawyer (*J. Ind. Eng. Chem.*, 1919, **11**, 1025—1028).—Determinations have been made of the freezing points of binary systems in which one component was 2:4:6-trinitro-*m*-xylene and the other a nitrotoluene, and also of ternary systems containing two of these nitrotoluenes and 2:4:6-trinitro-*m*-xylene. The cooling-curve method was used for the determinations. In the case of mixtures of trinitro-*m*-xylene with the nitrotoluenes the eutectic temperatures (corr.) were as follows: with 2:4:6-trinitrotoluene, 74·8° (corresponding with 8% of the trinitroxylene); with 2:4-dinitrotoluene, 67·7° (corresponding with 6% of trinitroxylene); and with *p*-nitrotoluene, 50·5° (corresponding with 2%). The binary eutectic temperature for the mono- and dinitro-toluenes (26·4°) was lowered to 25·7° by the addition of trinitroxylene, and a similar lowering was observed on adding trinitroxylene to binary mixtures of the other nitrotoluenes. The relationship between the composition and m. p. of mixtures is shown by the equation $\log_e x = -Q(T_0 - T)/RTT_0$, where Q represents the molecular heat of fusion, T_0 is the m. p. of the pure substance, T its m. p. in the presence of a second component, and x the molecular fraction of the melting component. The value of Q calculated from the points on the curve for trinitro-*m*-xylene and trinitrotoluene, $x = 0{\cdot}337$ and $T = 138{\cdot}1°$ C. or $411{\cdot}1°$ A., was found to be 9200 cals. Substitution of these values in the above equation gave $T = 2012{\cdot}7/4{\cdot}424 \log_{10} x$. This gave results agreeing well with the observed results in the case of mononitrotoluene, but in the case of the other two nitrotoluenes there was considerable deviation for the eutectic mixtures up to about 20% of trinitro-*m*-xylene. C. A. M.

The Nitrotoluenes. II. Refractive Indices of Mixtures of *p*-Nitrotoluene, 2 : 4-Dinitrotoluene, and 2 : 4 : 6-Trinitrotoluene. James M. Bell and Edmund O. Cummings (*J. Ind. Eng. Chem.*, 1919, **11**, 1028—1029).—The refractive indices of mixtures of *p*-nitrotolueue, dinitrotoluene, and triuitrotoluene were determined at 38—39°, and the results expressed in relation to the composition of the mixtures in a triangular diagram showing the lines of equal refractive index. The results, which were confined to mixtures freezing below 40° (the eutectic temperatures being about 17°), agreed in all but a few instances (within the limits of experimental error) with the values calculated by means of the formula $n=1{\cdot}542m+1{\cdot}572d+1{\cdot}580t$, where m, d, and t represent the respective weights of mono-, di-, and tri-nitrotoluene in a mixture. C. A. M.

The Conductivities of Iodoanilinesulphonic Acids. (Miss) Mary Boyle (T., 1919, **115**, 1505—1517).

Preparation of [Derivatives] of *p*-Toluenesulphonic Acid Halogenated in the Side-chain. Society of Chemical Industry in Basle (D.R.-P. 312959; from *Chem. Zentr.*, 1919, iv, 373—374).—*p*-Toluenesulphonic acids or their dry salts are treated at an elevated temperature with halogens or substances which yield halogens, and in the presence or absence of halogen carriers. ω-Chloro- or di-ω-chloro- or ω-bromo- or di-ω-bromo-toluene-*p*-sulphonic acids are obtained according to the amount of halogen used and the experimental conditions employed. The *sodium* salts of ω-chlorotoluene-*p*-sulphonic acid and ω-*o*-dichlorotoluene-*p*-sulphonic acid are particularly described. H. W.

New Halogenated Sulphones. A. Purgotti (*Ann. R. scuola superiore d'agr. in Portici*, 1915—1916, (2), **13**, 8 pp.).—The sulphones were obtained by the action of alkyl or aryl haloids on a boiling alcoholic solution of sodium *p*-chlorobenzenesulphinate for fourteen to twenty hours. Thus, methyl iodide yields p-*chlorophenylmethylsulphone*, slender, needle shaped, vitreous crystals, m. p. 57—58°, which is not reduced by nascent hydrogen or oxidised by permanganate. Ethyl bromide yields p-*chlorophenylethylsulphone*, white crystals, m. p. 260—261° (decomp. at a slightly higher temperature), which is very stable to oxidising and reducing agents. *iso*Propyl bromide yields p-*chlorophenylisopropylsulphone*, vitreous prisms, m. p. 226—227°, which is unaltered by oxidising or reducing agents. Ethylene dibromide yields *di*-p-*chlorophenylethylenedisulphone*, silky laminæ, m. p. 237—238°, which is not attacked by oxidising agents, but is converted into 2 mols. of *p*-chlorophenyl methyl sulphone by zinc and hydrochloric acid. p-*Chlorophenylbenzylsulphone*, prepared from benzyl chloride, forms white laminæ, and has m. p. 257—258°; oxidising agents change it into benzoic acid and *p*-chlorobenzenesulphonic acid. p-*Chlorophenyl* 2 : 4 : 6-*trinitrophenylsulphone*, pre-

pared from picryl chloride, forms a dense, brownish-red oil, which, after twenty-four hours, solidifies to a crystalline mass; after recrystallisation, this forms yellow, lustrous needles, m. p. 104—105°. If heated slowly it decomposes at about 200°, but if heated quickly explodes violently. CHEMICAL ABSTRACTS.

A Method for the Preparation of Aromatic Selenonic Acids. *o*- and *p*-Xyleneselenonic Acids. RICHARD ANSCHÜTZ JOSEF KALLEN, and KARL RIEPENKRÖGER (*Ber.*, 1919, **52**, [*B*], 1860—1875).—The xylenes react with 96% selenic acid (the preparation of which is described) in the presence of acetic anhydride at 0°, giving white crystals of the very hygroscopic selenonic acid. The position of the substituent has not been determined, but it is probable that one compound is p-*xylene*-2-*selenonic acid*, m. p. 95—96°, and the other o-*xylene*-4-*selenonic acid*, m. p. 108—110°. Salts of ten metals are described, as well as the corresponding salts of the sulphonic acids, most of which are new. Most attention is paid to the molecules of water of crystallisation, the numbers of which are set out in the following table:

Acid.	NH_3.	K.	Na.	Ba.	Mg.	Zn.	Ag.	Cu.	Ni.	Co.
p-Xyleneselenonic.....	0	0	4	3	8	10	1	10	7	9
„ sulphonic ...	0	1	1	0	8	10	1	5	7	9
o-Xyleneselenonic ...	0	0	4	3	0	6	0	6	5	5
„ sulphonic ...	0	0	5	2	5	5	0	6	6	5

J. C. W.

ωω'-Diarylparaffins and ω-Arylparaffincarboxylic Acids. W. BORSCHE (*Ber.*, 1919, **52**, [*B*], 2077—2085).—The author has applied Clemmensen's method of reduction to a number of mono- and di-ketones which had previously served as starting point in the preparation of ωω'-diarylparaffins (Borsche and Wollemann, A., 1913, i, 171). In general, it is found that αβ-unsaturated ketones yield only small quantities of the corresponding saturated hydrocarbons when reduced by amalgamated zinc and concentrated hydrochloric acid, large amounts of resin being formed. The corresponding saturated mono- and the saturated di-ketones, on the other hand, give satisfactory yields of the hydrocarbons. The method may also be successfully employed in the reduction of a number of ketonic acids.

αε-Dianisylpentane, a colourless, oily liquid, b. p. 264—266° 30 mm., is prepared by the reduction of αε-di-*p*-methoxyphenylpentane-γ-one by zinc and hydrochloric acid; the corresponding *phenol*, b. p. 300—301°/32 mm., is obtained by the reduction of *αε-di*-p-*hydroxyphenylpentan-γ-one*, colourless oil, b. p. 313—314° 14 mm., and yields a *tetranitro*-derivative, pale yellow crystals, m. p. 146—148° (decomp.). αζ-*Di*-m-4-*xylylhexane* forms colourless leaflets, m. p. 76—77°, b. p. 247—248°/20 mm. (formed from *αζ-di*-m-4-*xylylhexane*-*αζ-dione*, colourless needles, m. p. 125—126°, which results, together with m-4-*xyloylvaleric acid*, colourless needles, m. p. 98—99°, from the condensation of adipyl chloride

with *m*-xylene in the presence of aluminium chloride [compare Veckenstedt, *Inaug. Diss.*, Göttingen, 1911]). *αθ-Di*-m-4-*xylyloctane*, colourless needles, m. p. 63—64°, b. p. 253—254°/13 mm., is obtained from *αθ-di*-m-4-*xylyloctane-αθ-dione*, yellow needles, m. p. 78—79°. Reduction of *αι-di*-p-*tolylnonane-αι-dione*, slender, colourless needles, m. p. 78—79°, leads to the formation of *αι-di*-p-*tolylnonane*, m. p. 48—49°, b. p. 248—252°/18 mm. (*ω*-p-*toluoyloctoic acid* has m. p. 98°). *ακ-Di*-m-4-*xylyldecane-ακ-dione*, slender, intertwined needles, m. p. 61°, could not be reduced to the corresponding hydrocarbon by Clemmensen's or Paal's process.

The following acids have been prepared by Clemmensen's method from the ketonic acids or their esters: *γ*-p-*tolyl*-n-*butyric acid*, colourless leaflets, m. p. 58—59°, from *β*-*p*-toluoylpropionic acid; *γ*-*β-naphthyl*-n-*butyric acid*, colourless leaflets, m. p. 100° (*ethyl* ester, colourless oil, b. p. 216—218°/20 mm.); *ε-phenylhexoic acid*, b. p. 206—208°/30 mm.; *η-phenyloctoic acid*, colourless leaflets, b. p. 209—210°/14 mm.; *ι-phenyldecoic acid*, m. p. 41°, b. p. 228—230°/18 mm. (*ethyl* ester, b. p. 220—224°/20 mm.). It should be noted that in the reduction of the acids with amalgamated zinc and hydrochloric acid in the presence of a relatively small amount of alcohol, esterification of the organic acid frequently occurs to some extent.

The following products have been obtained from adipyl chloride and toluene, *p*-xylene, and mesitylene respectively: *αζ-di*-p-*tolylhexane-αζ-dione*, m. p. 144—145°, and *δ*-p-*toluoylvaleric acid*, m. p. 153—154°; *αζ-di*-p-3-*xylylhexane-αζ-dione*, m. p. 127—128°, and *δ*-p-3-*xyloylvaleric acid*, m. p. 132—133°; *αζ-dimesitylhexane-αζ-dione*, m. p. 102—103°, and *δ-mesitoylvaleric acid*, crystalline mass, b. p. 236°/13 mm. Glutaryl chloride and *m*-xylene yield *αε-di*-m-4-*xylylpentane-αε-dione*, m. p. 60—61°, and *γ*-m-*xyloylbutyric acid*, m. p. 118°. H. W.

Preparation of Nitro-compounds of Tetrahydronaphthalene and its Homologues. Tetralin G.m.b.H. (D.R.-P. 299014; from *Chem. Zentr.*, 1919, iv, 374).—Tetrahydronaphthalene, or its homologues, is treated with nitric-sulphuric acid or other nitrating mixtures which do not contain more than 25% of water in such a manner that the temperature does not exceed 50° in the first phases of the action. In these circumstances, oxidation and resinification are almost completely avoided. Tetrahydronaphthalene and nitric–sulphuric acids give a mixture of *α*- and *β-nitrotetrahydronaphthalene*, b. p. 121—128°/0·17 mm., which is also obtained when concentrated nitric acid (D 1·47) is gradually added to a solution of tetrahydronaphthalene in acetic anhydride, a mixture of acetic acid and acetic anhydride, or an indifferent solvent. A mixture of nitric acid (D 1·47, 160 parts) and sulphuric acid monohydrate (200 parts) yields 1 : 3-*dinitrotetrahydronaphthalene*, yellow crystals, m. p. 71—72°, which is oxidised to 3 : 5-*dinitrophthalic acid*, m. p. 226°, by moderately concentrated nitric acid. It decomposes when heated, and forms an explosive

mixture with potassium chlorate, ammonium nitrate, etc. It is converted by a mixture of fuming sulphuric and nitric acids into *trinitrotetrahydronaphthalene*, yellowish-white crystals, m. p. 80—81°. H. W.

Triphenylmethyl. XXIX. Diphenyl-α-naphthylmethyl. M. Gomberg and C. S. Schoepfle (*J. Amer. Chem. Soc.*, 1919, **41**, 1655—1676. Compare A., 1918, i, 111).—The investigation was undertaken with the object of preparing a compound possessing a considerably greater degree of dissociation than triphenylmethyl to determine whether this attribute would be accompanied by an enhancement of the various chemical characteristics of the latter, and to determine with a high degree of accuracy the molecular weight of the free radicle in various solvents covering a wide range of temperature in order to ascertain the influence of temperature on the molecular state of the free radicle.

Diphenyl-α-naphthylmethyl chloride, large, colourless crystals, m. p. 170—171°, is most conveniently prepared by the action of the calculated quantity of acetyl chloride on diphenylnaphthylcarbinol dissolved in benzene; the corresponding *bromide* has m. p. 165—166° (slight decomp.), whilst *diphenylnaphthyl ethyl ether* forms well-defined, colourless crystals, m. p. 132°. *Diphenyl-α-naphthylmethyl* is obtained by the action of molecular silver on a solution of the chloride in benzene, and forms practically colourless crystals, which gradually become pale yellow, m. p. about 135—137° after darkening at 130°. The radicle absorbs oxygen very rapidly, but in spite of the fact that the theoretical amount of the gas is absorbed, diphenylnaphthylmethyl, like triphenylmethyl, does not give the theoretical quantity of peroxide. It readily reacts with iodine, and an equilibrium is attained, $CPh_2{\cdot}C_{10}H_7 + I \rightleftharpoons CPh_2I{\cdot}C_{10}H_7$, when approximately 60% of the radicle has been changed; attempts to isolate the iodide were unsuccessful, but its formation is definitely established by the isolation of the corresponding *anilide*, m. p. 151°. When an excess of iodine is added to the solution of diphenylnaphthylmethyl, an unstable periodide separates as an oil. When treated with hydrogen chloride in benzene solution, the free radicle is converted to the extent of more than 80% into diphenylnaphthylmethane and diphenylnaphthylmethyl chloride, the remainder being transformed into a *polymeride*, $C_{46}H_{34}$, very fine, colourless crystals, m. p. 234—235°, the molecular weight of which appears to be abnormal. Reduction by hydrogen in the presence of platinum black converts diphenylnaphthylmethyl into diphenylnaphthylmethane.

Attempts are described to prepare additive compounds of the free radicle with ethyl and ethyl amyl ethers, amyl formate, ethyl acetate, amyl acetate, ethyl chloroacetate, ethyl valerate, acetone, dipropyl ketone, methyl butyl ketone, acetonitrile, propionitrile, benzene, toluene, xylene, and hexane respectively; in no case did addition take place, the behaviour of diphenylnaphthylmethyl in this respect being in marked contrast with that of triphenylmethyl.

Solutions of diphenylnaphthylmethyl are only slowly affected by exposure to light; since, however, the products formed contain considerable quantities of diphenylnaphthylmethane, it seems probable that the reaction occurs on lines similar to those with triphenylmethyl, but far more slowly.

The molecular weight of diphenylnaphthylmethyl has been determined by the cryoscopic method in nitrobenzene, *p*-bromotoluene, *p*-dichlorobenzene, *p*-chlorobromobenzene, and naphthalene respectively, thus giving a temperature range from +6° to 80°; it has been found that the temperature as well as the concentration has a marked influence on the dissociation of free radicles, whilst the nature of the solvent appears to exert but slight influence. Increase in the concentration of the solution invariably causes an increase in the molecular weight, which is interpreted as shifting the equilibrium, $C_{10}H_7{\cdot}CPh_2{\cdot}CPh_2{\cdot}C_{10}H_7 \rightleftharpoons 2C_{10}H_7{\cdot}CPh_2$, in favour of the bimolecular form. At a temperature of about 60°, diphenylnaphthylmethyl is shown to be present entirely in the unimolecular form, but above this temperature the molecular weight suffers a further decrease, the cause of which has not been established. H. W.

The Fluorene Series. I. Adolf Sieglitz (*Ber.*, 1919, **52**, [*B*], 1513—1517).—Thiele has shown that fluorene condenses with benzaldehyde, anisaldehyde, cinnamaldehyde, and furfuraldehyde in the presence of sodium ethoxide (A., 1900, i, 347; 1906, i, 571). Derivatives of other aldehydes are now described.

9-o-*Methylbenzylidenefluorene* forms flat, colourless needles and prisms, m. p. 109·5°, soluble in concentrated sulphuric acid with violet colour; *picrate*, orange needles, m. p. 138—139°. 9-p-*Methylbenzylidenefluorene* forms flat, colourless crystals, m. p. 97·5°; *picrate*, yellow, m. p. 117—118°. 9:9′-*Terephthalylidenedifluorene*, $C_6H_4(CH{:}C_{13}H_8)_2$, crystallises in golden-yellow, glistening leaflets, m. p. 209—210°, olive-green in sulphuric acid. The 9-*chlorobenzylidenefluorenes* are as follows: *ortho*, yellow needles, m. p. 176°, dark brown in sulphuric acid; *meta*, pale yellow prisms and pyramids, m. p. 90·5°, deep green in sulphuric acid; *para*, pale yellow, m. p. 149·5°, deep blue in sulphuric acid. 9-m-*Bromobenzylidenefluorene* forms yellow needles, m. p. 92—93°, deep green in sulphuric acid. J. C. W.

Transformation of Anilines into *cyclo*Hexylamines and the Isomerism of these Bases. A. Skita and W. Berendt (*Ber.*, 1919, **52**, [*B*], 1519—1535).—Hitherto, the catalytic reduction of anilines has given very unsatisfactory results, for there is a great tendency for ammonia to be evolved and secondary amines to result in consequence. With colloidal platinum as the catalyst, however, and by varying the concentration, temperature, and proportion of hydrochloric acid present, it is possible so to control the reduction that the primary *cyclo*hexylamine is the sole product or the secondary base the main product. Reduction with colloidal platinum is about thirty times as rapid as with spongy platinum,

which is probably due, not only to the greater surface available, but to the fact that the bases have no time to "poison" the catalyst before the action is over. In any case, the catalyst must be employed in unusual concentrations, about 0·6% for the monoamines and double this for diamines.

The catalyst is prepared by shaking a solution of hydrochloroplatinic acid, containing gum arabic, with hydrogen, after inoculation with a little colloidal platinum.

The following reductions are described. *Aniline:* A mixture containing 1·5 grams of platinum (from hydrochloroplatinic acid), 1·5 grams of gum arabic, 0·09 mol. (8·37 grams) of aniline, 110 c.c. of glacial acetic acid, and 120 c.c. of water (designated the "normal mixture"), was reduced in three hours at 21°, giving *cyclo*hexylamine, b. p. 135° (40·3%), and di*cyclo*hexylamine, b. p. 250° (59·7%). At 55—60° the same mixture was reduced in twenty-five minutes, the yield of secondary base being 78·4%. With the addition of 10 c.c. of concentrated hydrochloric acid, the mixture was reduced in two and a-half hours at 21°, giving primary *cyclo*hexylamine only. *Alkylanilines:* At about 40—50° good yields of the simple secondary amines are obtained, but at 80°, and with more concentrated solutions of the catalyst, the monoalkylanilines give 40—55% yields of tertiary amines. The dialkylanilines give almost the same results under both conditions. cyclo*Hexylmethylamine*,

$$C_6H_{11}\cdot NHMe,$$

has b. p. 145—147°, and its *benzoyl* derivative has m. p. 85—86°; *cyclo*hexyldimethylamine has b. p. 160—161° (A., 1904, i, 661); *cyclo*hexyldiethylamine has b. p. 193° (*ibid.*), di*cyclohexylmethylamine* has b. p. 265°, and its lemon-yellow *picrate* has m. p. 140°; di*cyclohexylethylamine* has b. p. 268°, and its *picrate* has m. p. 138°.

Toluidines.—The "normal mixture," containing *p*-toluidine, plus 5 grams of hydrogen chloride, was reduced at 25° in four hours, the product being 4-methyl*cyclo*hexylamine, b. p. 150—151° (Gutt, A., 1907, i, 508). This is apparently a mixture of *cis*- and *trans*-isomerides, for it yields two *benzoyl* derivatives, the α-form having m. p. 180° (corr.) (*ibid.*), and the β-form, which is the more soluble of the two in dilute alcohol, having m. p. 116°. At 52° the "normal mixture" is reduced in seventy-five minutes, giving a 68% yield of *4:4′-dimethyldicyclohexylamine*, b. p. 133°/10 mm. This gives two *nitrosoamines*, the α-form, m. p. 128—129° (corr.), crystallising from moderately strong alcohol, and the β-form, m. p. 90—91° (corr.), from more dilute alcohol. With *m*-toluidine the "normal mixture" was reduced in five hours at 23—26°, to 55·6% of primary amine, and 44·4% of secondary base, but at 55° the absorption of hydrogen was complete in thirty minutes, and the yield of secondary amine was 79·1%. 3-Methyl*cyclo*hexylamine has b. p. 150—151° (*ibid.*), and forms two *benzoyl* derivatives, the α-form having m. p. 127° (corr.) and the β-form m. p. 98·5° (corr.). 3:3′-Dimethyldi*cyclo*hexylamine has b. p. 172—173° (Wallach, A., 1893, i, 115). In the case of *o*-toluidine the yields with the "normal mixture"

were 83·8% primary and 16·2% secondary amine at 23°, and 58% secondary base at 55°. 2-Methyl*cyclo*hexylamine, b. p. 150—151°, hydrochloride, m. p. 269°, forms two *benzoyl* derivatives, *α*-, m. p. 146° (corr.) (Gutt, *loc. cit.*), and *β*-, m. p. 107° (corr.). 2:2′-*Dimethyldi*cyclo*hexylamine* has b. p. 273—274°, forms a *hydrochloride*, m. p. 284°, and yields two *picrates*, *α*-, tetrahedra, m. p. 184° (corr.), and *β*-, delicate needles, m. p. 153° (corr.).

Nitroanilines.—*m*-Nitroaniline is mainly reduced to *m*-phenylenediamine if insufficient catalyst is used, but a mixture containing 6·9 grams of base, 4 grams of colloidal platinum, 3 grams of gum arabic, 4 grams of hydrogen chloride, 150 c.c. of glacial acetic acid, and 130 c.c. of water was reduced at 55° so rapidly that heat was developed, and a 62% yield was obtained of *cyclo*hexylene-1:3-diamine, b. p. 193—194°, *platinichloride*, yellow needles (Merling, A., 1894, i, 177). *p*-Nitroaniline, under similar conditions, gave a 45% yield of *cyclo*hexylene-1:4-diamine, b. p. 181°, *platinichloride*, yellow crystals (von Baeyer, A., 1889, 1147).

In most of the reductions the hydrogen is kept under 3 atm. pressure. J. C. W.

Halogenalkylated Aromatic Amines. IV. Julius von Braun and Georg Kirschbaum (*Ber.*, 1919, **52**, [*B*], 1716—1724. Compare A., 1918, i, 107, 269, 406).—When methyl-*β*-bromoethylaniline is boiled with hydrochloric acid, it is converted into *methyl-β-chloroethylaniline*, $NMePh{\cdot}CH_2{\cdot}CH_2Cl$, which is a very pale yellow oil, b. p. 134°/13 mm., and forms a yellow *picrate*, m. p. 107°, a *methiodide*, colourless leaflets, m. p. 125°, and a *p-nitroso*-compound, emerald leaflets, m. p. 69°, which may be oxidised to *p-nitromethyl-β-chloroethylaniline*, $NO_2{\cdot}C_6H_4{\cdot}NMe{\cdot}CH_2{\cdot}CH_2Cl$, a greenish-brown, crystalline powder, m. p. 90°, and reduced to *methyl-β-chloroethyl-p-phenylenediamine*, an oil which yields an *acetyl* derivative, m. p. 131°. The reactivity of the halogen atom is not so great as in the case of the bromo-derivative, but it is still quite considerable. For example, the base reacts with sodium benzoate to form *methyl-β-benzoyloxyethylaniline* [*β-methylanilinoethyl benzoate*], m. p. 48—49° (*picrate*, m. p. 164°), and with ethyl sodiomalonate to give *ethyl β-methylanilinoethylmalonate*, $NMePh{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CO_2Et)_2$, a viscous oil, b. p. 190°/mercury pump.

The replacement of one halogen by another may be illustrated still further. The chloro-derivative yields the bromo-compound when boiled with hydrobromic acid, and both may be converted into *methyl-β-iodoethylaniline*, colourless crystals, m. p. 43—44° (*hydriodide*, m. p. 139°), by boiling with hydriodic acid. The phenomenon has been put to practical use in the preparation of a *γ*-halogenopropyl base. Methylaniline does not react in the desired way with ethylene or trimethylene dichlorides, and the product obtained by heating it with trimethylene dibromide cannot be distilled. By boiling the crude product with hydrochloric acid, however, the above exchange of halogens takes place, and *methyl-β-*

chloropropylaniline may be isolated as a very pale yellow oil, b. p. 140—144°/13 mm. This base forms a *platinichloride*, m. p. 154—156°, a *picrate*, m. p. 113°, a *methiodide*, m. p. 107—108°, and a dark, oily *nitroso*-compound, and it reacts with sodium to give oily N:N′-*diphenyldimethylhexamethylenediamine*,

$$NMePh\cdot[CH_2]_6\cdot NMePh$$

(*picrate*, m. p. 82°), and with trimethylamine to form the oily *quaternary chloride*, $NMePh\cdot C_3H_6\cdot NMe_3Cl$ (*platinichloride*, m. p. 211°). When boiled with hydrobromic acid, *methyl-β-bromopropylaniline* is formed, and this may now be distilled; b. p. 150—155°/12 mm., 117—121°/0·01 mm.; *picrate*, m. p. 94—95°; *platinichloride*, m. p. 132°.

The halogenoethyl bases yield 1-methyldihydroindole when heated with aluminium chloride, but the halogenopropylanilines do not give quinoline derivatives. J. C. W.

Mechanism of the Grignard Reaction. Julius von Braun and Georg Kirschbaum (*Ber.*, 1919, **52**, [*B*], 1725—1730).—In the first communication on bromoalkylated anilines (A., 1918, i, 107) it was shown that the magnesium compounds react with aldehydes and ketones, but that the ketones are regenerated on treating the products with water. It was suggested that the primary products can be represented thus:

$$\begin{matrix} R \\ H \end{matrix}\!\!>\!C\!:\!O\!<\!\!\begin{matrix} MgX \\ R' \end{matrix} \qquad \text{and} \qquad R_2\!:\!C\!:\!O\!<\!\!\begin{matrix} MgX \\ R' \end{matrix}.$$

Apparently, then, when R′ is $NMePh\cdot CH_2\cdot CH_2-$, rearrangement into $RR'CH\cdot O\cdot MgX$ is possible in the case of aldehydes, but there are steric hindrances in the way of the formation of $R_2R'C\cdot O\cdot MgX$. When the heavy NMePh-group is further away, however, as in the case of methyl-γ-bromopropylaniline (preceding abstract), the necessary rearrangement is possible even in the ketone series.

The following compounds are obtained from magnesium γ-methylanilinopropyl bromide: (1) with *iso*valeraldehyde, N:N′-diphenyldimethylhexamethylenediamine (*ibid.*), and *methyl-δ-hydroxy-γ-methylheptylaniline*, $NMePh\cdot C_3H_6\cdot CH(OH)\cdot CH_2\cdot CHMe_2$, a viscous oil, b. p. 154—156°/12 mm. (*picrate*, m. p. 161°; *platinichloride*, m. p. 210°); with acetone, methylpropylaniline, and *methyl-δ-hydroxy-δ-methylamylaniline*, a very viscous oil, b. p. 164—170°/13 mm. (*platinichloride*, m. p. 193°); with *cyclo*hexanone, the base,

$$\begin{matrix} NMePh\cdot C_3H_6 \\ HO \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{matrix}\!\!>\!CH_2,$$

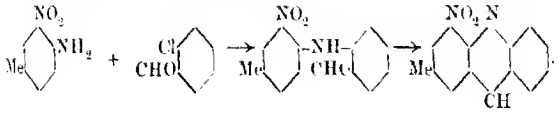
which seems to lose water slowly on heating.

The steric hindrance seems to be connected with the presence of nitrogen also, for the Grignard compound from γ-phenyl-*n*-butyl bromide (A., 1913, i, 612) behaves quite normally with acetone, yielding *sec.*-butylbenzene and βη-diphenyloctane (*ibid.*), but chiefly *ε-phenyl-β-methylhexan-β-ol*, $C_{11}H_{15}MePh\cdot CH_2\cdot CH_2\cdot CMe_2\cdot OH$, a very viscous liquid, b. p. 135°/11 mm. J. C. W.

5-Nitro-2-amino-1-methyl-4-*iso*propylbenzene. C. E. ANDREWS (U.S. Pat. 1314923).—To introduce a nitro-group into aminocymene in a position para to the amino-group, the amino-group is first protected against the action of the nitrating medium by boiling with glacial acetic acid for fifteen to twenty hours. Nineteen parts of the solid acetylaminocymene thus obtained are dissolved in 98% sulphuric acid (84 parts) and the solution thus formed is nitrated with a mixture of 98% sulphuric acid (13 parts) and 70% nitric acid (10 parts), while the reacting substances are kept at 0°. By pouring the products into water containing ice a yellow precipitate of *p*-nitroacetylaminocymene is obtained. This may be treated directly for reduction of the nitro- to the amino-group by heating with iron and hydrochloric acid, and the acetyl group may subsequently be removed by treatment with concentrated hydrochloric acid, from which, on keeping, the hydrochloride of 2:5-diamino-1-methyl-4-*iso*propylbenzene separates as crystals. The intermediate product (5-amino-2-acetylamino-1-methyl-4-*iso*propylbenzene) may be diazotised and coupled with a hydroxy-aromatic compound in alkaline solution, after which the acetyl group can be removed and the 2-amino-group can then be caused to react with hydroxy- or amino-aromatic compounds. This procedure is preferable to reacting on tetrazotised diaminocymene with aromatic hydroxy-derivatives, where two different second components are to be employed in producing bisazo-dyes. CHEMICAL ABSTRACTS.

4-Amino-5-methyl-2-*iso*propylbenzenesulphonic Acid. C. E. ANDREWS (U.S. Pat. 1314927).—Aminocymene or its sulphate is heated for about ten hours with 98% (or fuming) sulphuric acid at about 205° until a test portion gives no reaction for the free amine on making it alkaline. The solid reaction mass is broken up and dissolved in hot sodium hydroxide solution, purified by filtration through "decolorising carbon," and acidified to obtain 4-amino-5-methyl-2-*iso*propylbenzenesulphonic acid.
CHEMICAL ABSTRACTS.

Action of *o*-Chlorobenzaldehyde on Chloroanilines and Amines of Fluorene and Anthraquinone. FRITZ MAYER and IRENE LEVIS (*Ber.*, 1919, **52**, [*B*], 1641–1652).—It has already been found that under certain conditions *o*-chlorobenzaldehyde does not react with ortho-substituted anilines to form the usual azomethines, but condenses according to the following scheme, taking an actual example (A., 1918, i, 36):



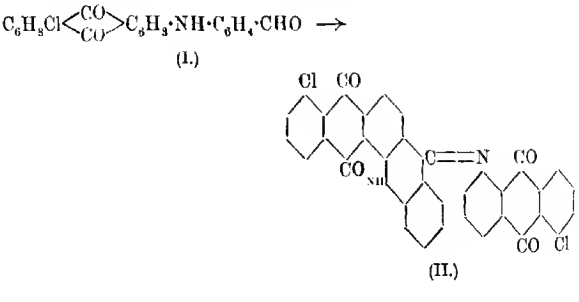
The reaction with chloroanilines and aminofluorenes has now been

examined, but these are found to give only the azomethines or no condensation products at all. Certain anthraquinone derivatives, however, yield the more complex products.

In the experiments, the azomethines were obtained by condensing the components in warm dilute alcohol, and the other condensations were tested by heating the substances in nitrobenzene or naphthalene at 210—220° with a little copper powder and anhydrous sodium carbonate.

The chloroanilines gave the following compounds: 2:2′-*dichlorobenzylideneaniline*, m. p. 112—113°; 3:2′-*dichlorobenzylideneaniline*, two forms, m. p. 104° and m. p. 39—40°, the former passing into the latter on fusion and inoculation with crystals of the low melting form; 4:2′-*dichlorobenzylideneaniline*, m. p. 65—68°; 2:4:2′-*trichlorobenzylideneaniline*, m. p. 97—98°; a *trichloro-2′-chlorobenzylideneaniline*, m. p. 109°, from technical trichloroaniline, the pure 2:4:6-trichloroaniline giving no condensation product. 2-Chloro-4-nitroaniline yields 2:2′-*dichloro-4-nitrobenzylideneaniline*, yellow crystals, m. p. 155—156°. 4-Chloro-2-nitroaniline only reacts in naphthalene solution, and then gives a small yield of 3-*chloro*-1-*nitroacridine*, pale yellow needles, m. p. 219—221°. 3-Chloro-*p*-toluidine gives 2:2′-*dichloro*-4-*methylbenzylideneaniline*, m. p. 68—70°. 2-Chloro-5-nitrobenzaldehyde and *p*-chloroaniline yield 4:2′-*dichloro*-5′-*nitrobenzylideneaniline*, m. p. 124—125°. 2:4-Dinitroaniline and 1-aminoanthraquinone do not condense with 2-chloro-5-nitrobenzaldehyde. 2-Aminofluorene and 2-aminofluorenone (Diels, A., 1901, i, 521) yield 2:2′-*chlorobenzylideneaminofluorene*, m. p. 128—129, and 2:2′-*chlorobenzylideneaminofluorenone*, m. p. 153—155°. 1-Nitro-2-aminofluorene does not react, but 2-nitro-7-aminofluorene (A., 1902, i, 758) forms 2-*nitro*-7:2′-*chlorobenzylideneaminofluorene*, m. p. 230°.

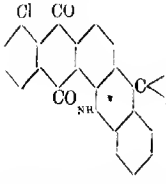
5-Chloro-1-aminoanthraquinone yields o-5-*chloro*-1-*anthraquinonylaminobenzaldehyde* (5-*chloro*-1-o-*aldehydoanilinoanthraquinone*) (I), reddish-violet crystals, which condenses with more 5-chloro-1-aminoanthraquinone in boiling nitrobenzene, under the influence of mercuric sulphate, giving the *compound* (II).



(I.)

(II.)

The aldehyde (I) also condenses to the esters of 1:2-o-*chlorophthalyl*-5 : 10-*dihydroacridol* (annexed formula), which in the free state is apparently a brownish-violet powder, when heated with sulphuric acid at 115—120°, or with acetic acid saturated with hydrogen chloride. The *hydrogen sulphate* forms dark violet crystals, and the *hydrochloride* is violet.



1-Chloroanthraquinone-2-aldehyde (Ullmann, A., 1916, i, 484) condenses with 1-aminoanthraquinone to form 1:1′-*anthraquinonylaminoanthraquinone-2-aldehyde*,

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_2\cdot NH\cdot C_6H_2(CHO)\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_4,$$

as a violet-red powder, which condenses further with 1-aminoanthraquinone to give a violet *compound* of the formula

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_2\langle\begin{matrix}NH\\C\end{matrix}\rangle C_6H_2\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_4$$
$$\|$$
$$N\cdot C_6H_3\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_4$$

Heated with sulphuric acid, the aldehyde also forms the violet *sulphonate* of 1:2:8:9-*diphthaloyl*-5 : 10-*dihydroacridyl hydrogen sulphate*,

$$\left[C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_2\langle\begin{matrix}NH\\CH\end{matrix}\rangle C_6H_2\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_4\right]_2H_2SO_4.$$
$$|$$
$$SO_3H$$

J. C. W.

Diphenylamine. H. Rogers (U.S. Pat. 1314538).—Diphenylamine is formed by heating a mixture of aniline with about 1% of ammonium bromide in an autoclave, preferably for about forty-eight hours under a condensing column, which is arranged to permit release of the ammonia evolved without loss of aniline. A temperature of about 300° gives the best results. Bromine itself may be used as a catalyst instead of ammonium bromide, or other bromine compounds may be used, for example, aniline hydrobromide, bromobenzene, or magnesium bromide. It is practically essential that about 1% of water should be present in the reaction zone. After heating in the autoclave, the reaction product is fractionated. The first fraction, distilling up to 200°, consists mainly of unchanged aniline, together with a small amount of diphenylamine, and is stored for re-digestion with a fresh amount of catalyst.

The second fraction, distilling at 200—300°, consists of a mixture of aniline with a larger amount of diphenylamine. The larger part of the diphenylamine can be recovered from this second fraction by redistillation. The main quantity of the diphenylamine produced is collected in the fraction which distils at 300° and above. A tarry residue is left in the still, from which the catalyst may be recovered. An apparatus is described. CHEMICAL ABSTRACTS.

The Isomerism between Real and Pseudo-haloid Salts. A. HANTZSCH (*Ber.*, 1919, **52**, [*B*], 1544—1572).—Two distinct chromoisomerides have been found in the case of certain -onium haloids, especially iodides, and a study of their absorption and transformations has led the author to postulate the following characteristics of real and pseudo-haloids. (1) *The genuine haloids.*—The halogen is in ionic union with the -onium complex, that is, is in the "outer sphere" according to Werner's teaching; the salts are optically identical with their ions. Thus, $[NR_4]X$, $[PR_4]X$, $[AsR_4]X$, $[SR_3]X$, $[OR_3]X$. (2) *The ψ-haloids.*—The halogen is directly united to the central atom; the absorption is much greater than in the case of the normal haloids, and therefore the ψ-forms are often yellow. They are expressed by the old formulæ for the salts, thus, $R_4{=}N{-}I$, etc. The tendency for the normal salts to change into the less stable ψ-forms is favoured by higher temperatures and non-ionising solvents, such as chloroform and *s*-tetrachloroethane, and depends on the nature of the ions. Of the anions, iodine has the greatest effect and chlorine scarcely any. The most effective cations are those in which the central atom is in an unsaturated ring system, as in pyridinium and pyroxonium salts. Next come the most phenylated ions, such as triphenylbenzyl- and triphenylmethyl-phosphonium, but with the alkylated ions, even such as tetrabenzylarsonium, the salts show little tendency to rearrangement. The isomerisation is a time reaction, and therefore a solution in chloroform generally represents an equilibrium, which is displaced not only by rise of temperature, but also by dilution. This suggests participation of the apparently indifferent solvent, and in the case of 1-ethylpyridinium iodide the fact is revealed that both salts form solvates with chloroform, the stable, normal form giving a less stable solvate than the labile ψ-modification. Ionising solvents have absolutely no optical effect on the normal haloids.

These views are chiefly based on a study of 1-ethylpyridinium iodide and 4-methoxy-2:6-dimethylpyroxonium iodide (compare this vol., i, 72). For the practical details, which are accompanied by much discussion, the original should be consulted.

J. C. W.

Attempted Preparation of New Compounds of Nitrogen. H. STAUDINGER and JULES MEYER (*Helv. Chim. Acta*, 1919, 2, 608—612).—According to Werner's conception, the co-ordination

number of nitrogen is four, so that only four atoms or radicles can be united directly to a nitrogen atom. Should it be possible, however, for the nitrogen atom to be united directly with five groups, it is to be expected that the most stable compounds would be formed when the atom is attached to five carbon atoms. The only known compound of this type is triphenylmethyltetramethylammonium, $CPh_3 \cdot NMe_4$, described by Schlenk and Holtz (A., 1916, i, 385), the peculiar instability of which is possibly due to the presence of the triphenylmethyl group. The present communication describes a number of unsuccessful attempts to obtain further compounds of similar structure.

The action of dimethylaniline oxide (2 mols.) on diphenylketen (1 mol.) leads to the formation of dimethylaniline and benzophenone, whilst with molar proportions of the reagents the products are dimethylaniline and diphenylketen oxide, the dimethylaniline oxide behaving in each case as an oxidising agent. With phenylcarbimide and dimethylaniline oxide, carbon dioxide, dimethylaniline, and amorphous substances of high molecular weight are formed. Triethylamine, dimethylaniline, and triphenylamine could not be caused to react with diphenyldiazomethane or with phenylazide.

H. W.

A Peculiar Transformation of Methylallylaniline *N*-Oxide. Jakob Meisenheimer (*Ber.*, 1919, **52**, [*B*], 1667—1677).—Methylallylaniline is converted into *methylallylaniline N-oxide*,

$$CH_2{:}CH \cdot CH_2 \cdot NPhMe{:}O,$$

by the action of perbenzoic acid in benzene, being isolated as the *picrate*, $OH \cdot NPhMe(C_3H_5) \cdot O \cdot C_6H_2(NO_2)_3$, which crystallises in stout, yellow forms, m. p. 121° (decomp.). If the benzene solution is extracted with 10% hydrochloric acid and the extract is carefully mixed with sodium hydroxide, the oxide is liberated as a very soluble, unstable substance, but if the alkaline solution is heated by means of a current of steam it soon becomes turbid, and a very pale yellow, mobile oil distils over. This oil, b. p. 97°/14—16 mm., is shown to be *N-phenylmethyl-O-allylhydroxylamine*, $CH_2{:}CH \cdot CH_2 \cdot O \cdot NMePh$, by the following series of reactions, but no explanation of its formation from the isomeric methylallylaniline *N*-oxide is offered. The transformation is conditioned by the allyl group, for no other amine oxides are known to behave in this way. The most convenient way to obtain the oil is to oxidise the methylallylaniline with Caro's acid at 30—35°, extract impurities with ether, and then add concentrated sodium hydroxide and distil in steam.

The oil is hydrolysed by boiling with hydrochloric acid according to the scheme:

$$C_3H_5 \cdot O \cdot NMePh \begin{cases} \nearrow NHMePh + CH_2{:}CH_2 \cdot CHO \\ \searrow CH_2{:}CH \cdot CH_2 \cdot OH + NMePhCl \end{cases} \longrightarrow C_6H_4Cl \cdot NHMe.$$

Of the products, acraldehyde was identified by its odour and conversion into lead acrylate, methylaniline as its somewhat reddish-yellow *picrate*, m. p. 144·5°, and acetyl derivative, *p*-chloromethylaniline as its greenish-yellow *picrate*, m. p. 153°, and acetyl derivative (Chattaway and Orton, T., 1901, **79**, 465), and possibly *o*-chloromethylaniline, a picrate being obtained in bundles of greenish-yellow needles, m. p. 133°. When heated with zinc dust and acetic acid, the oil yields methylaniline and allyl acetate. The latter was hydrolysed, and the alcohol characterised by conversion into *allyl* p-*nitrobenzoate*, m. p. 28°. Reduction by Skita's method (colloidal platinum protected with gum arabic) gives rise to *N-phenylmethyl-O-propylhydroxylamine*, an almost colourless oil, b. p. 92—94°/12 mm., which is hydrolysed by dilute sulphuric acid to propaldehyde, methylaniline, and *p*-hydroxymethylaniline.

J. C. W.

Action of Nitrous Acid on β-Phenylhydroxylamine. Eug. Bamberger and Alex. Landau (*Ber.*, 1919, **52**, [*B*], 1837—1842).—A more complete study of this subject, with particular reference to the by-products (compare A., 1894, i, 412). Starting with 79·7 grams of phenylhydroxylamine, 86·5 grams of the nitroso-compound, NO·NPh·OH, were obtained as a precipitate. The filtrate was extracted with ether, and the aqueous solution added to β-naphthol in sodium hydroxide, giving a quantity of dye corresponding with 2·9 grams of benzenediazonium hydroxide. The ethereal solution was saturated with ammonia gas, filtered (residue *A*), shaken with 12% ammonia solution (*B*), dried, and evaporated, leaving 0·69 gram of nitrosobenzene. The residue *A* consisted of ammonium salts, chiefly of nitrosophenylhydroxylamine, but also of phenylnitroamine, NO_2·NHPh, the latter salt being also present in solution *B*. The phenylnitroamine was isolated by dissolving *A* in water, adding sodium carbonate and permanganate in the cold to oxidise the nitrosophenylhydroxylamine to nitrosobenzene, filtering, extracting with ether after acidifying, and shaking the extract with dilute ammonia. On evaporating the ammoniacal solution, 0·11 gram of phenylnitroamine was obtained.

The nitroamine is most probably formed by the rearrangement of the nitrosophenylhydroxylamine under the influence of nitrous acid, for when a solution of the potassium salt of the latter is acidified in the presence of sodium nitrite, a trace of nitroamine is produced.

J. C. W.

Phenols as Mordant Dyes. Richard Möhlau (*Ber.*, 1919, **52**, [*B*], 1730—1734).—Those phenols which are constitutionally capable of forming internally complex salts are found to impart more or less stable shades to mordanted wool, as the following table indicates:

	Al.	Fe.	Cr.
†α-Anthrol	Brown	Brown	Yel.-brown
†β-Anthrol	Yel.-brown	Yel.-brown	Yel.-brown
Catechol	—	*Pale grey	Yel.-grey
1 : 2-Dihydroxynaphthalene.	—	Grey.-brown	Yel.-brown
†1 : 8- ,,	Black	Brown-black	Brown.-black
†Phenanthraquinol	—	—	Red.-brown
1 : 2-Dihydroxyanthracene .	Yel.-brown	Yel.-brown	Yel.-brown
†2 : 3- ,,	Red.-brown	Red.-brown	Red.-brown
Pyrogallol	—	Dark grey	Yel.-grey
Salicylic acid	—	*Pale red	—
2 : 3-Dihydroxynaphthoic acid	—	*Red.-violet	—
Protocatechuic acid	—	*Grey.-violet	Pale grey
Gallic acid	—	,,	Yel.-grey
Methyl gallate	—	,,	Pale grey
†1 : 2-Dihydroxynaphthalene-4-sulphonic acid	Yel.-brown	Yel.-brown	Red.-brown

(1) With the exception of those marked *, the colours are unchanged by light and air after thirty days, and also by boiling with 2% soap solution.

(2) Those marked † give colours which are quite stable towards boiling *N*-hydrochloric acid.

No effect is produced by phenol, α- and β-naphthols, resorcinol, quinol, 1:3- and 2:7-dihydroxynaphthalenes, or *m*- and *p*-hydroxybenzoic acids. J. C. W.

Acetylation of Nitrophenols in Presence of Catalysts. G. E. Hoeffelman (*Proefschrift Delft*, 1919, 134 pp.; from *Chem. Weekblad*, 1919, **16**, 904).—The author has investigated the acetylation of trinitrophenol, *op*-dinitrophenol, *p*-nitrophenol, and *o*-nitrophenol by acetic anhydride both in presence and absence of catalysts such as ferric chloride, zinc chloride, concentrated sulphuric acid, and pyridine. The following points are discussed: (1) The nature of the reactions without a catalyst. (2) Are catalytic reactions definite or does inactivity occur? (3) The relationship between reaction constant and amount of catalyst. (4) The cause of inactivity in certain reactions and the determination of a limit when it occurs. (5) The influence of various catalysts on the acetylation of several nitrophenols. W. J. W.

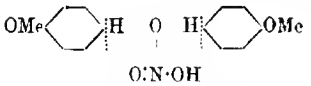
Action of Nitric Acid on Phenolic Ethers. Kurt H. Meyer and Hans Gottlieb Billroth (*Ber.*, 1919, **52**, [*B*], 1476—1489).—It has been known for some time that by-products with very intense colours are formed during the nitration of phenolic ethers. For example, Decker and Salonina isolated a deep blue compound from thymol ethyl ether (*A.*, 1902, i. 767). It is now shown that the substances can be isolated as perchlorates by diluting the nitration products with ice-water, filtering, and adding the solution to perchloric acid. The salts yield diphenylamine derivatives on reduction, and are best regarded (with Decker) as quinonoid salts of substituted diphenylhydroxylamine-*N*-oxides, $NPh_2O{\cdot}OH$.

This is the derivative of nitric acid which corresponds with diphenylarsinic acid, but attempts to isolate it or its metallic salts have been unsuccessful. In the case of the anisyl derivative, the attempts have led to the isolation of dianisylnitric oxide,

$$NO(C_6H_4\cdot OMe)_2,$$

which is more stable than diphenylnitric oxide (Wieland and Offenbächer, A., 1914, i, 955).

In the action of nitric acid on phenolic ethers, there is obviously a choice of two reactions, the ordinary nitration and the present reaction, represented by the annexed formula. Methyl groups, and especially methoxy-groups, in the meta-position are favourable to this reaction, as they are to the coupling process with diazo-compounds, but whilst the phenomenon seems to be most characteristic of phenolic ethers, it is not entirely confined to this class, for resorcinol behaves in a similar manner.



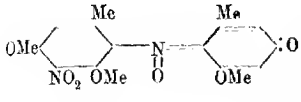
The quinonoid *perchlorate* of *di*-p-*anisylhydroxylamine* N-*oxide*, $OMe\cdot C_6H_4\cdot N(:O):C_6H_4:O<^{Me}_{ClO_4}$, crystallises from acetone on the addition of light petroleum in coppery needles containing $1H_2O$, which is lost at 50° in a vacuum desiccator. The solutions are red in deep layers and pure blue in thin layers or when very dilute. Reduction to di-*p*-anisylamine may be effected by means of stannous chloride or sodium iodide, and followed titrimetrically in each case. The perchlorate is reduced to *di*-p-*anisylnitric oxide* by treatment with an alkali, or sodium iodide, or zinc powder, in acetone, or, most conveniently, by dissolving it in pyridine and gradually adding water. The oxide crystallises in needles or platelets, and has the appearance of copper powder, m. p. 150° (decomp.). Its reduction by sodium iodide may be followed volumetrically, and it is re-oxidised to the deep violet salts by bromine or concentrated mineral acids.

Phenetole yields the violet-brown *perchlorate* of diphenetylhydroxylamine *N*-oxide, decomp. 114°, and copper-coloured diphenetylnitric oxide. *m*-Tolyl methyl ether gives the *perchlorate* of 5:5′-dimethoxydi-*m*-tolylhydroxylamine *N*-oxide, dark crystals with $1H_2O$, decomp. 142°. *o*-Tolyl methyl ether gives a mere trace of coloured salt. *m*-5-Xylyl methyl ether yields the dark brown *perchlorate* of 5:5′-dimethoxydi-*m*-2-xylylhydroxylamine *N*-oxide.

Resorcinol dimethyl ether gives the *perchlorate* of 2:4:2′:4′-*tetramethoxydiphenylhydroxylamine* N-*oxide*, $C_{16}H_{17}O_6NCl.H_2O$, as a violet-brown powder, decomp. 178°. The deep green solutions of this become cornflower-blue on adding two equivalents of stannous chloride, and colourless with four equivalents, the final product being 2:4:2′:4′-*tetramethoxydiphenylamine*, which forms large, colourless crystals, m. p. 71°, and yields a *nitroso*-derivative, m. p. 111°. Resorcinol diethyl ether gives the corresponding *perchlorate*.

$C_6H_3(OEt)_2{\cdot}N(:O):C_6H_3(OEt){\cdot}OEt{\cdot}ClO_4$, in very dark green, glistening needles, decomp. 131°.

Orcinol dimethyl ether yields the *perchlorate* of 3:5:3′:5′-*tetramethoxydi-o-tolylhydroxylamine* N-*oxide*, dark violet-brown needles, $1H_2O$, decomp. 121°, and 3:5:3′:5′-*tetramethoxydi-o-tolylamine*, m. p. 106°, and its *nitroso*-compound, m. p. 186°. If the product of the nitration of orcinol dimethyl ether is left with water, a red *compound*, decomp. 150°, is deposited, probably represented by the annexed formula.



Phloroglucinol trimethyl ether gives rise to the *perchlorate* of 2:4:6:2′:4′:6′-*hexamethoxydiphenylhydroxylamine* N-*oxide*, dark blue crystals, decomp. 189°. J. C. W.

Aromatic Nitro-derivatives. X. Nitration of Thymol. M. Giua (*Gazzetta*, 1919, **49**, ii, 158—166).—The author's investigations on the trinitro-compounds obtained on nitrating thymol and its ethyl and methyl ethers confirm the conclusions of Armstrong and Rennie (*Chem. News*, 1883, **47**, 115), Maldotti (A., 1901, i, 80), and Larter (P., 1901, 183), namely, that Lallemand's trinitrothymol and its ethers (*Compt. rend.*, 1857, **37**, 498; 1857, **38**, 1022; 1860, **43**, 375, 459) are in reality trinitro-*m*-cresol and its ethers.

Further, the trinitro-compound obtained by nitrating either the methyl or the ethyl ether of thymol reacts with hydrazine hydrate in alcoholic solution, giving rise to 2:4:6-trinitro-*m*-tolylhydrazine (compare this vol., i, 100). Phenylhydrazine also reacts with these compounds, yielding the same product (compare this vol., i, 98).

Nitration of the ethyl ether of thymol, dissolved in sulphuric acid, by means of fuming nitric acid at a moderately low temperature and for a short time gives the ethyl ether of dinitro-*m*-cresol, m. p. 96—97° (compare Staedel and Kolb, A., 1891, 186). Further nitration of the latter yields the ethyl ether of 4:5:6-trinitro-*m*-cresol, m. p. 75°. In the ethyl ether of dinitro-*m*-cresol obtained from thymol, one of the nitro-groups occupies the position formerly occupied by the *iso*propyl group, which is evidently eliminated by the action of the nitric acid. T. H. P.

Transformation of *cyclo*Hexanones into Catechols. Guido Cusmano (*Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 30—33).—*Methylisopropylcatechol*, $C_6H_3(OH)_2{\cdot}CH_3{\cdot}C_3H_7$, obtained either as such by heating monobromo-Buchu-camphor above its melting point or as diacetyl derivative by heating the same bromo-compound with acetic anhydride and anhydrous sodium acetate in a reflux apparatus, crystallises in colourless prisms, m. p. 48°, b. p. about 270°, gives a green coloration with ferric chloride in alcoholic solution, and in aqueous solution, especially rapidly in presence of alkali,

undergoes oxidation to a hydroxythymoquinone, m. p. about 165°; this oxidation is favoured also by organic bases, such as aniline, which gives a violet-blue coloration. With phenylcarhimide, it yields the crystalline *phenylurethane*, $C_{24}H_{24}O_4N_2$, m. p. 170°.

T. H. P.

Molybdic Acid-Catechol Compounds. R. F. Weinland and Fritz Gaisser (*Zeitsch. anorg. Chem.*, 1919, **108**, 231—247).—It has been found that catechol reacts with molybdates in aqueous solution to form coloured compounds in which an atom of the oxygen of the molybdate molecule has been displaced by the catechol residue ($C_6H_4O_2$). The simplest of these compounds is prepared by mixing solutions of ammonium molybdate and catechol, in the proportion of 1 molecule of the former to from 6 to 12 of the latter, and allowing the solution to evaporate, when large, deep red crystals in the form of four- or six-sided columns with sharp pyramidal ends are obtained. They can be recrystallised from water, methyl, or ethyl alcohol, and in each case have the composition represented by the formula $(NH_4)H[MoO_3(C_6H_4O_2)],\frac{1}{2}H_2O$. The aqueous solution is gradually decolorised by acids, and the compound is also decomposed by alkalis. Corresponding salts of the alkali metals could not be prepared, but by the action of pyridine on the ammonium compound two new compounds were obtained, an ammonium pyridine compound, brownish-red needles, easily soluble in water and methyl alcohol, less easily in ethyl alcohol, to which the formula $(NH_4)(C_5H_5NH)[MoO_3(C_6H_4O_2)],\frac{1}{2}H_2O$, is given, and a pyridine salt. The latter can also be prepared by heating an aqueous solution of molybdic anhydride (1 mol.), catechol (1 mol.), and pyridine (2 to 3 mols.). It forms orange-red aggregates of microscopic needles, m. p. 60°, and its composition corresponds with the formula $(C_5H_5N)H_2[MoO_3(C_6H_4O_2)],1{\cdot}5H_2O$. An anhydrous quinoline salt corresponding in composition with the above ammonium pyridine compound, and a tetramethylammonium compound having the formula $NMe_4H[MoO_3(C_6H_4O_2)]$ were also prepared. An anhydrous dipyridine salt was also obtained.

A dipyridine–dicatechol molybdate was obtained from a solution in which one molecular proportion of molybdic acid was heated with two of catechol and five to ten of pyridine. It forms bright red, six-sided tables, and can be recrystallised from methyl alcohol unchanged, but not from water or ethyl alcohol. It has the composition $(C_5H_5NH)_2[MoO_2(C_6H_4O_2)_2]$, m. p. 137°. In presence of more than two molecular proportions of catechol, the last compound crystallises with the excess of catechol in varying quantities. The compounds isolated contained: (1) $C_6H_4(OH)_2,2H_2O$, m. p. 53°; (2) $\frac{1}{2}C_6H_4(OH)_2$, m. p. 142°; (3) $1{\cdot}5C_6H_4(OH)_2,2H_2O$, m. p. 138°.

E. H. R.

***m*-Anisyltellurium Compounds.** Karl Lederer (*Ber.*, 1919, **52**, [*B*], 1989—1992. Compare A., 1917, i, 134).—Di-*m*-anisyl telluride has been prepared by the action of magnesium *m* anisyl iodide on tellurium dibromide; it is purified by conversion into the

crystalline dibromide and reduction of the latter with magnesium methyl iodide.

Di-m-*anisyltelluride*, $Te(C_6H_4\cdot OMe)_2$, is a pale yellow oil, b. p. 247—252°/34—36 mm., which gives rise to the following *di*-m-*anisyltelluronium* compounds in the usual way; *dichloride*, slender, felted needles, m. p. 162—163°; *dibromide*, small, felted needles, m. p. 185—186°; *di-iodide*, minute, golden-yellow needles, m. p. 167—168° (decomp.), after softening at 163°; *oxide*,

$$TeO(C_6H_4\cdot OMe)_2,$$

amorphous powder, which softens at 69° and is completely molten at 90°; *methiodide*, not obtained in the pure condition. It also forms *additive* compounds with the mercuric haloids as follows: *iodide*, $Te(C_6H_4\cdot OMe)_2,HgI_2$, yellow needles, m. p. 122—123°, after softening at 120°; *bromide*, needles, m. p. 114—115° (decomp.), after softening at 108°; *chloride*, colourless, amorphous powder, which softens at 83° and is completely molten at about 89°.

H. W.

A Simple and Convenient Way to Prepare Aromatic Selenium Compounds. A. Schoeller (*Ber.*, 1919, **52**, [*B*], 1517—1518).—Instead of treating diazotised anilines with alkali selenides or selenocyanates, which involve the use of hydrogen selenide in their preparation, the same results may be obtained with alkali polyselenides. A reagent is best obtained by fusing black selenium with potassium hydroxide and dissolving the product in ice-water. About twice the theoretical quantity is applied to the diazonium compound, 75% of the excess being precipitated during the reaction and the remainder recovered from the mother liquors of the organic selenide by the action of sulphur dioxide.

Benzenediazonium chloride gives an 80% yield of diphenyl selenide, whilst diazotised anthranilic acid gives a mixture of diselenide (85%) and monoselenide (compare Lesser and Weiss, A., 1913, i, 1184; 1915, i, 445).

J. C. W.

Cholesterol. XXVIII. Transformation of Cholesterol into Cholanic Acid. A. Windaus and K. Neukirchen (*Ber.*, 1919, **52**, [*B*], 1915—1919).—It has often been surmised that cholic acid, $C_{24}H_{40}O_5$, is intimately connected with cholesterol, $C_{27}H_{46}O$, especially as they give similar colour reactions, but a direct proof has necessitated several years of experiment. A clue was first found in the fact that cholesterol yields acetone on oxidation with chromic acid, whereas cholic acid does not, that is, the difference in the carbon content is that of an *iso*propyl group (A., 1918, ii, 22). Cholanic acid, $C_{24}H_{40}O_2$, which has the three hydroxyl groups of cholic acid replaced by hydrogen, behaves in the same way (Wieland and Weil, A., 1912, i, 831). This led the authors to attempt the removal of the *iso*propyl group from a suitable cholesterol derivative, and as a substance in which there are no complications left in the nuclear parts of the molecule, they have chosen cholestane, $C_{27}H_{48}$, the product obtained by the chemical reduction of cholesterol.

When cholestane is oxidised by chromic acid in glacial acetic acid it gives an acid which is remarkably like cholanic acid, but on comparing it with a specimen provided by Wieland it proves to be an isomeride after all. The isomerism is akin to that which exists between cholesterol, dihydrocholesterol, and cholestane on the one hand and coprosterol and ψ-cholestane on the other, for when ψ-cholestane is oxidised in the same way the product is the true cholanic acid.

Cholanic acid has m. p. 164° and its ethyl ester crystallises in long needles, m. p. 93—94°; iso*cholanic acid* has m. p. 162° (the mixture begins to soften at 150° and is clear at 155°), the *methyl* ester has m. p. 79—80°, and the *ethyl* ester crystallises in leaflets, m. p. 79°. J. C. W.

Xanthosterol, a Crystalline Compound from the Bark of Xanthoxylum Budrunga. H. Dieterle (*Arch. Pharm.*, 1919, **257**, 260—263).—*Xanthosterol*, $C_{28}H_{40}O$, obtained in about 0·25% yield by extracting the bark of *Xanthoxylum Budrunga* with light petroleum, forms slender, white needles, m. p. 213—214°. Its molecule contains a hydroxyl group, and it forms a *benzoyl* derivative, $C_{35}H_{44}O_2$, fine needles, m. p. 261—265°; an *ethylcarbonato*-derivative, $C_{28}H_{39}O{\cdot}CO_2Et$, white, nodular crystals, m. p. 175—176°; a *methylcarbonato*-derivative, $C_{28}H_{39}O{\cdot}CO_2Me$, greasy leaflets, m. p. 191—193°; and a *bromo*-derivative, $C_{28}H_{39}OBr$, colourless needles, m. p. 169—170°.

Its reactions indicate xanthosterol to be an alcohol related to lupeol (compare Likiernik, A., 1891, 551, 1446; Sack and Tollens, A., 1904, i, 1011) and to alstol (Sack and Tollens, *loc. cit.*). With concentrated sulphuric acid, it yields a yellow coloration, which changes to brown with a slight green fluorescence on heating. When its chloroform solution is treated with concentrated sulphuric acid, the chloroform gradually becomes pale yellow with a green fluorescence and the acid brown; evaporation of this chloroform solution leaves a violet residue. Addition of concentrated sulphuric acid, drop by drop, to a solution of xanthosterol in acetic anhydride gives a stable, red coloration.

The bark of *Xanthoxylum Budrunga* contains also an alkaloid, to be studied later. T. H. P.

Condensation of Formaldehyde with some Unsaturated Compounds. H. J. Prins (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 51—56. Compare A., 1917, i, 685; 1918, i, 261).—The condensation of formaldehyde with styrene, anethole, camphene, and cedrene has been studied. The reaction with styrene yields β-phenyltrimethylene glycol (*loc. cit.*), b. p. 176°/13 mm., D_4^{18} 1·1161, n_D^{19} 1·54267, and its *methylene ether*, b. p. 128—130°, D_4^{18} 1·1111, n_D^{18} 1·53063. Anethole yields the *methylene ether* of *p-methoxyphenylbutylene glycol*, b. p. 168—170°/13 mm., D_4^{16} 1·1197, n_D^{16} 1·53438. On boiling a solution of trioxymethylene in acetic acid with camphene for three days, *homocamphenol ace-*

tate is produced, an oil, h. p. 124—128°/13 mm., D_4^{19} 1·0013, n_D^{19} 1·48209. A mixture of cedrene with an equivalent quantity of formaldehyde in 15% sulphuric acid and acetic acid on stirring for three days yields *homocedrenol*, h. p. 168—171°/13 mm., D_4^{19} 1·0270, n_D^{15} 1·51826, along with products of considerably higher boiling point. J. F. S.

Manufacture of Synthetic Drugs [Adrenaline]. Nanayoshi Nagai (Brit. Pat. 118298).—Equimolecular proportions of nitromethane and diacetylprotocatechualdehyde, prepared by the interaction of protocatechualdehyde and acetyl chloride or acetic anhydride, are condensed at ordinary temperatures in presence of a dilute solution of a weak alkali to diacetoxyphenylnitroethanol, $C_6H_3(OAc)_2\cdot CH(OH)\cdot CH_2\cdot NO_2$. The crystalline product is collected, washed free from protocatechualdehyde with ether, and treated with acetic acid and zinc dust in presence of a 35% formaldehyde solution containing a molecular equivalent of formaldehyde, whereby simultaneous reduction and methylation take place with the production of diacetoxyphenylmethylaminoethanol, $C_6H_3(OAc)_2\cdot CH(OH)\cdot CH_2\cdot NHMe$. The zinc is precipitated from the reaction mixture as sulphide, and to the filtered solution the requisite amount of hydrochloric acid is added to effect hydrolysis and to combine with the liberated base. On evaporation at a low temperature in a vacuum, crystals of dihydroxyphenylmethylaminoethanol hydrochloride (adrenaline hydrochloride) are obtained. G. F. M.

Benzoylation of some Hydroxy- or Amino-aromatic Compounds. Frédéric Reverdin (*Helv. Chim. Acta*, 1919, **2**, 729).—The author has recently succeeded in effecting certain difficult benzoylations by benzoyl chloride in the presence of a little concentrated sulphuric acid (A., 1918, i, 536); the latter substance has been employed previously for benzoylation with benzoic anhydride. H. W.

Manufacture of β-Halogen-ethylaminobenzoic Acid Esters. Société Chimique des Usines du Rhone (Brit. Pat. 128553).—β-Halogen-ethyl-*p*-aminobenzoic esters of the general formula $XCH_2\cdot CH_2\cdot NH\cdot C_6H_4\cdot CO_2R$, where X is a halogen and R an alkyl group, are obtained by treating the corresponding hydroxyethyl compounds (Brit. Pat. 128552) with halogenating agents, such as phosphorus or sulphur haloids, thionyl chloride, or bromide, etc., preferably in the presence of a diluent such as benzene or a tertiary amine. *Ethyl β-chloroethyl-p-aminobenzoate* is a crystalline substance, melting at 69°, and boiling at 183° at 3 mm. pressure. [See also *J. Soc. Chem. Ind.*, 1920, 43A.] G. F. M.

Manufacture of β-Alkylaminoethylaminobenzoic Alkyl Esters. Société Chimique des Usines du Rhone (Brit. Pat. 128554).—β-Alkylaminoethyl-*p*-aminobenzoic esters are obtained by heating for several hours in a closed vessel at a temperature of

about 100° a mixture of an alkylamine and a β-halogenethyl-*p*-aminobenzoic ester (see preceding abstract). *Ethyl β-diethylamino-ethylaminobenzoate*, $NEt_2 \cdot CH_2 \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot CO_2Et$, prepared thus from diethylamine and ethyl β-chloroethyl-*p*-aminobenzoate, is an oil giving a water-soluble *monohydrochloride* when evaporated to dryness with the requisite quantity of dilute hydrochloric acid. On recrystallisation from alcohol the hydrochloride gives white needles melting at 156°. G. F. M.

Manufacture of Substituted Benzoic Acid Esters. Société Chimique des Usines du Rhone (Brit. Pat. 128912).—Di-β-halogen-ethyl-*p*-aminobenzoic acid esters of the general formula $N(CH_2 \cdot CH_2X)_2 \cdot C_6H_4 \cdot CO_2R$, where X is a halogen and R an alkyl group, are prepared in the same way as the monohalogen esters (see Brit. Pat. 128553, preceding page), starting from the di-β-hydroxyethylaminobenzoic esters (see Brit. Pat. 128552). *Ethyl di-β-chloroethyl-p-aminobenzoate* melts at 53° and boils at 215°/3 mm. with slight decomposition. By the method described in Brit. Pat. 128554 (preceding abstract) the dichloro-esters may be converted into di-β-alkylaminoethyl-*p*-aminobenzoic esters. Thus diethylamine and ethyl di-β-chloroethylaminobenzoate give *ethyl tetraethyldiaminodiethyl-p-aminobenzoate*,

$$N(CH_2 \cdot CH_2 \cdot NEt_2)_2 \cdot C_6H_4 \cdot CO_2Et,$$

which forms a crystalline mass, soluble in dilute hydrochloric acid to give a dihydrochloride; this on crystallisation from alcohol forms white needles, m. p. 194—195°. G. F. M.

Some Derivatives of *p*-Dimethylaminobenzoic Acid. H. Rivier and Ch. Schneider (*Helv. Chim. Acta*, 1919, **2**, 717—719). —*Ethyl* p-*dimethylaminobenzoate* crystallises in colourless leaflets, m. p. 67—68°. *p*-Dimethylaminobenzanilide has m. p. 181—182° (compare Staudinger and Endle, A., 1917, i, 646), and is converted by phosphorus pentachloride into the *hydrochloride* of p-*dimethylaminobenzanilide iminochloride*, $NPh:CCl \cdot C_6H_4 \cdot NMe_2,HCl$. p-*Dimethylaminothiobenzanilide*, from the anilide and phosphorus pentasulphide, forms yellow needles, m. p. 170—171°. H. W.

The Replacement of Halogen attached to a Ring Carbon Atom by other Substituents. I. Replacement of Halogen by the Carboxyl Group. Karl W. Rosenmund and Erich Struck (*Ber.*, 1919, **52**, [*B*], 1749—1756).—Halogen atoms in aromatic compounds can be directly replaced by carboxyl groups by heating the compounds with aqueous or aqueous-alcoholic potassium cyanide and a little cuprous cyanide for some hours at about 200° in strong, sealed tubes. Good results have been obtained with halogen derivatives of benzene (mono- and di-), toluene, aniline, nitrobenzene, phenol, carboxylic acids, naphthalene, and thiophen. Apparently, copper is the unique catalyst in such condensations, for in the well-known and easier case of the replacement of halogen by the amino-group, silver, nickel, cobalt, zinc, and cadmium salts are almost ineffective.

The following examples are given. Benzoic acid from bromobenzene, *p*-toluic acid from *p*-bromotoluene, *p*-aminobenzoic acid from *p*-bromoaniline, terephthalic acid from *p*-dibromobenzene, anisic acid from *p*-bromoanisole, the three phthalic acids from the three bromobenzoic acids, α-naphthoic acid from α-bromonaphthalene, thiophen-2-carboxylic acid from 2-bromothiophen, and o-3 : 4-*dimethoxybenzoylbenzoic acid*, $C_6H_3(OMe)_2 \cdot CO \cdot C_6H_4 \cdot CO_2H$, small needles, m. p. 208—209°, from 2-*bromo*-3′ : 4′-*dimethoxybenzophenone* (o-*bromobenzoylveratrole*), stout plates, m. p. 154—155°, this being obtained by the Friedel and Crafts's reaction.

The bebaviour of chloronitrobenzenes towards potassium cyanide was investigated by Richter (1871–1873), who found that the meta- and para-compounds gave cblorobenzoic acids wben heated with the cyanide solutions at 200° whereas *o*-chloronitrobenzene was unaffected. It is now found that the last isomeride yields *o*-nitrobenzoic acid if a little cuprous cyanide is present and the temperature is not allowed to rise above 195°, whereas at about 210° phthalic acid and another substance, free from nitrogen and chlorine, are the products. J. C. W.

Preparation of Tyrosine for the Tyrosinase Reaction. M. W. Beijerinck (*Chem. Weekblad*, 1919. **16**, 1494–1495).—A small quantity of trypsinum activum is added to a 10% solution of pepton siccum, the mixture being put in a stoppered flask and shaken with a little chloroform to prevent decomposition by anaërobe bacteria. The flask is kept in a thermostat at 40°, with occasional agitation. After ten to fourteen days the peptone will be converted into tyrosine. *Euphorbia lathyris*, *Beta vulgaris*, *Morus nigra*, and *Microspira tyrosinatica* are recommended as sources of tyrosinase. W. J. W.

Intra- and Inter-molecular Active Forces and their Significance in Atomic Rearrangements, in Racemisation, and in Asymmetric Synthesis. Emil Erlenmeyer (*Biochem. Zeitsch.*, 1919, **97**, 198—245).—On reducing active phenylbromolactic acid with zinc in hot alcoholic solution one half of it passes into phenyl-β-lactic acid and the other half into cinnamic acid. When the zinc salts of the acids are decomposed with dilute sulphuric acid and the cinnamic acid is extracted with ether, it is found to be optically active, rotating in the same direction as the active phenylbromolactic acid from which it is derived. That this activity of the cinnamic acid is not due to contamination with phenyl-lactic acid is shown by experiments in which repeated extractions with water still leave an active cinnamic acid. This is further confirmed by the fact that a mixture of *i*-cinnamic acid with active phenyl-lactic acid of the same optical activity as that shown by the active cinnamic acid differs from it in other respects. The active cinnamic acid obtained as above shows an asymmetric crystalline form. On brominating a mixture of the zinc salts of *d*-phenyl-lactic acid and *i*-cinnamic acid the *l*-dibromide of cinnamic acid is obtained. On the other hand, *l*-phenyl-lactic acid and *i*-cinnamic

acid yield the *d*-dibromide. The reduction products of *l*- and *d*-phenylbromolactic acids, likewise, yield dibromides of cinnamic acid of the opposite rotation to the phenylbromolactic acids employed. Further experiments with *d*-tartaric acid, *l*-chlorosuccinic acid, *l*-mandelic acid, and *i*-cinnamic acid have shown the following:—

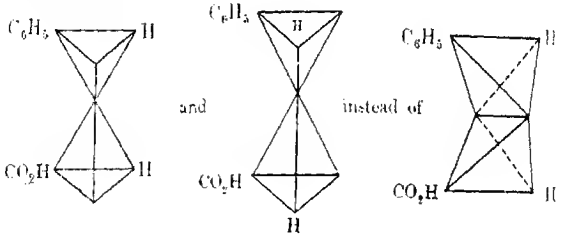
i-Cinnamic acid with *d*-tartaric acid yields *l*-cinnamic acid + Br_2 —> *d*-dibromide.

i-Cinnamic acid with *l*-chlorosuccinic acid yields *d*-cinnamic acid + Br_2 —> *l*-dibromide.

i-Cinnamic acid with *l*-mandelic acid yields *d*-cinnamic acid + Br_2 —> *l*-dibromide.

On treating *d*-cinchonine with *i*-cinnamic acid, *l*-cinnamic acid is obtained, and on bromination the *d*-dibromide is formed.

As the geometrical isomeric formula of cinnamic acid with the double bond cannot account for the active cinnamic acids, the author suggests a stereoisomeric structure with free unsaturated affinities thus:



He also suggests that the activation of the cinnamic acid in the above reactions is brought about by the "induction" influence of the asymmetric active components involved in the reactions, namely, the phenyl-lactic acids, *d*-tartaric acid, *l*-chlorosuccinic acid, etc.

The stereoisomerism of the optically active *iso*valeric acid obtained by the author and Landsberger from the brucine salt of methyl-ethylmalonic acid is also discussed. S. S. Z.

The Explanation of the Reciprocal Action of Asymmetric Substances with an Asymmetric Carbon Atom on Cinnamic and *allo*-Cinnamic Acids as Based on the Author's Isomerism Theory of the Ethylene Derivatives. Emil Erlenmeyer (*Biochem. Zeitsch.*, 1919, **97**, 245—255).—Applying the theory advanced in the preceding paper, the author discusses the action of some asymmetric substances on cinnamic and *allo*-cinnamic acids. The stereoisomeric formulæ of storax-α-cinnamic acid, storax-β-cinnamic acid, triclinic cinnamic acid, *allo*cinnamic acid, *iso*cinnamic acid (Liebermann), and *iso*cinnamic acid (Erlenmeyer, sen.) are discussed. S. S. Z.

Walden's Inversion. EMIL ERLENMEYER (*Biochem. Zeitsch.*, 1919, **97**, 255—261).—A theoretical paper. Walden's inversion is discussed in the light of the author's "induction" theory described in the preceding abstracts. S. S. Z.

Concerning the Force Emanating from Asymmetric Molecules and its Significance in Biochemistry. EMIL ERLENMEYER (*Biochem. Zeitsch.*, 1919, **97**, 261—311).—A theoretical paper. A lengthy exposition of the author's theory as to the stereoisomerism of ethylene derivatives and the "induction" influence of asymmetric active compounds (see preceding abstracts). Many observations already made in stereochemistry and biochemistry are discussed in the light of the new hypotheses.

S. S. Z.

Compounds of Molybdic Acid with Aromatic *o*-Hydroxy-Acids (Salicylic Acid and α-Hydroxynaphthoic Acid). R. F. WEINLAND and KURT ZIMMERMANN (*Zeitsch. anorg. Chem.*, 1919, **108**, 248—266).—It has been found that salicylic acid and α-hydroxynaphthoic acid combine with molybdic acid to form a series of coloured complex compounds. The complex acids themselves could not be isolated, but a number of pyridine, quinoline, and tetramethylammonium salts were prepared in crystalline condition. No compounds are formed between molybdic acid and *m*- or *p*-hydroxybenzoic acids. The evidence indicates that only the hydroxy-group of the organic acid interacts with the molybdic acid, not the carboxyl group.

By heating together in aqueous solution molybdic anhydride, salicylic acid, and pyridine in the molecular proportions 1:7:7, a deep yellow salt crystallising in thick, irregular, six-sided tables was obtained having the composition

$$4[MoO_2(O{\cdot}C_6H_4{\cdot}CO_2)_2]H_2{\cdot}9C_5H_5N{\cdot}4H_2O$$

(No. 1). When prepared in methyl-alcoholic solution, the same salt was obtained anhydrous. It cannot be recrystallised unchanged. Quinoline and tetramethylammonium salts of the same complex acid were prepared, and were all yellow. The corresponding pyridine salt containing α-hydroxynaphthoic acid is yellow. This is a complex acid salt containing 15 molecules of hydroxynaphthoic acid to 7 of molybdic acid and 13 of pyridine (No. 5). When this is heated with methyl alcohol, it is changed into the normal salt, $MoO_2(O{\cdot}C_{10}H_6{\cdot}CO_2)_2(H{\cdot}C_5H_5N)_2{\cdot}5H_2O$ (No. 6). When the compound No. 1 is heated with methyl alcohol, a new compound crystallises which has the composition

$$6[C_7H_4O_2(Mo_2O_7)]H_2{\cdot}7C_5H_5N{\cdot}3CH_3{\cdot}OH$$

(No. 11). This compound contains the new acid,

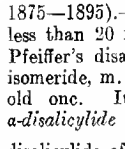
$$[C_6H_4(CO_2)Mo_2O_7]H_2.$$

The same anion appears to be present in a flesh-red compound which is formed by heating the pyridine salt No. 1 with water, and has the formula $8[C_7H_4O_2(Mo_2O_7)]H_2{\cdot}9C_5H_5N$ (No. 10). A similar flesh-coloured salt is obtained when No. 11 is heated in water; this has the composition $[C_7H_4O_2(MoO_3)_2]C_5H_5N{\cdot}H_2O$ (No. 12). By

heating the salt No. 5 with water, a yellowish-grey compound is obtained having the composition $[C_{11}H_6O_2(MoO_3)_2],C_5H_5N$ (No. 13).

Sodium, potassium, and ammonium salts of salicylomolybdic acid were also prepared. These were brownish-red compounds of very complex constitution, and appear to be double salts of monosalicylomolybdic acid, $[MoO_3{\cdot}O{\cdot}C_6H_4{\cdot}CO_2]H_2$, and disalicylomolybdic acid, $[MoO_2(O{\cdot}C_6H_4{\cdot}CO_2)_2]H_2$. E. H. R.

A New Disalicylide. Richard Anschütz [with Hans Jansen, Alfred Lublin, and Georg Metzges] (*Ber.*, 1919, **52**, [*B*], 1875—1895).—By the distillation of *o*-acetoxybenzoic acid under less than 20 mm. pressure, the author has obtained Einhorn and Pfeiffer's disalicylide, m. p. 200° (A., 1901, i, 712), and a new isomeride, m. p. 213°, which is less soluble in chloroform than the old one. It is found that the new isomeride, designated *α-disalicylide* (small, glistening prisms, m. p. 213°), is the normal disalicylide of the formula $C_6H_4\langle^{O{\cdot}CO}_{CO{\cdot}O}\rangle C_6H_4$, whereas the older, *β-disalicylide*, is probably represented by the annexed formula.



When distilled under reduced pressure, each passes to a slight extent into the other, but under atmospheric pressure they both give xanthone and carbon dioxide. Several other salicylic acid derivatives give the same pair of disalicylides when carefully distilled under reduced pressure, namely, tetrasalicylide, polysalicylide, diplosal (salicoylsalicylic acid), acetyldiplosal (*o*-2-acetoxybenzoyloxybenzoic acid, D.R.-P. 236196), and 2:2′-diacetoxybenzoic anhydride (from aspirin, by the action of thionyl chloride and pyridine, D.R.-P. 201329).

The α-disalicylide reacts with boiling alcohols to give the esters of diplosal; *methyl* o-2-*hydroxybenzoyloxybenzoate* (*methyl salicoylsalicylate*), $OH{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CO_2Me$, has m. p. 86—87°, and the *ethyl* ester, m. p. 59°, agreeing with specimens made by the action of alcoholic hydrogen chloride on diplosal. The β-disalicylide is much more stable towards alcohols. When heated with methyl alcohol at 150° for six hours, it is partly converted into methyl salicylate. Similarly, the α-isomeride reacts with ammonia in chloroform solution about five times as fast as the β-form, giving the *ammonium disalicoylimide*,

$$(HO{\cdot}C_6H_4{\cdot}CO)_2N{\cdot}NH_4.$$

This is a canary-yellow powder which may be obtained from methyl salicylate, through the amide and imide (Schulerud, A., 1881, 42). The ammonium salt has been converted into the following salts: *silver*, $(HO{\cdot}C_6H_4{\cdot}CO)_2N{\cdot}Ag$; *calcium*, $CaX_2,2H_2O$; *strontium*, $SrX_2,3H_2O$; *barium*, BaX_2,H_2O; *mercuric*, HgX; *cupric*, CuX; and *lead*, PhX. α-Disalicylide also reacts with aniline and *p*-toluidine at about 100°, giving *disalicoylanilide*,

$$NPh(CO{\cdot}C_6H_4{\cdot}OH)_2,$$

m. p. 165°, and *disalicoyl*-p-*toluidide*, m. p. 149°. J. C. W.

Isomerism of [Methyl] *o*-Benzoylbenzoate. A. Hantzsch (*Ber.*, 1919, **52**, [*B*], 1572—1573).—McMullen (A., 1916, i, 560) doubted the existence of isomerism in the case of methyl *o*-benzoylbenzoate because he could not obtain the ψ-form described by Meyer (A., 1904, i, 747). Hantzsch points out that he was successful in isolating this isomeride (A., 1916, i, 399). J. C. W.

Oxidative Degradation of Dehydro*iso*fenchoic Acid [Dehydro*iso*fenchocamphoric Acid]. N. J. Toivonen (*Annalen*, 1919, **419**, 176—216).—The experiments were originally undertaken with the object of elucidating the composition of dehydro-*iso*fenchoic acid; meanwhile, this has been accomplished by other methods (compare Aschan, A., 1913, i, 198), and the paper mainly gives an account of an instance of abnormal oxidation by permanganate in alkaline solution.

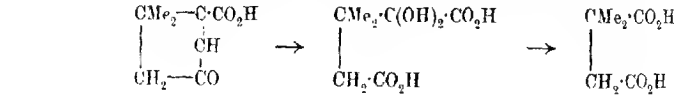
dl-Dehydro*iso*fenchoic acid was prepared by the successive action of phosphorus pentachloride and bromine on *dl-iso*fenchoic acid, conversion of the product into the ethyl ester, removal of hydrogen bromide from the latter by means of quinoline, and subsequent hydrolysis; it has m. p. 190—191°, and is soluble in water at 25° to the extent of 0·1061 gram in 100 grams. The ethyl ester has b. p. 131—134°/9—10 mm., 260—262°/772 mm., D_4^{20} 1·0121, n_D^{20} 1·45738. The monoethyl ester (β-form?) is a colourless, viscous liquid, b. p. 168—171°/9 mm., D_4^{20} 1·0730, whilst a second *modification* (α-form?) has b. p. 178—180°/15 mm., m. p. 50—51°, D_4^{20} 1·0737, n_D^{22} 1·47232. Attempts to convert the acid into an anhydride by means of acetyl chloride were unsuccessful, and it was not isomerised by a mixture of glacial acetic and hydrochloric acids (D 1·2). It did not unite with bromine. Hydrogen bromide, on the other hand, readily combined with it, yielding an *acid*, $C_{10}H_{15}O_4Br$, m. p. 267° (decomp.), which was not dehydrated by acetyl chloride, and, on energetic reduction, gave *r-cis-iso*-fenchoic acid. (The investigation of this action is not yet completed.) d-*Dehydroisofenchoic acid*, prepared similarly to the *dl*-acid, forms monoclinic needles and leaflets, m. p. 170—171°, $[\alpha]_D^{25}$ +30·28° in alcoholic solution, and is soluble in water to the extent of 0·3761 gram in 100 grams at 25°. The *diethyl* ester is a colourless, mobile liquid, b. p. 123°/6 mm., 261—262°/772 mm., D_4^{20} 1·0130, n_D^{21} 1·45892, $[\alpha]_D^{21}$ −36·69°. The *monoethyl* ester (β-form?) has b. p. 164°/8 mm., D_4^{20} 1·0760, n_D^{21} 1·46931, $[\alpha]_D^{20}$ +40·26°, whilst the corresponding *α-variety* (?) has b. p. 169—170°/8 mm., m. p. 46—47°, $[\alpha]_D^{19}$ +19·71° in alcoholic solution. l-*Dehydroisofenchoic acid* has m. p. 170—171°, $[\alpha]_D^{20}$ −30·43° in alcohol, and dissolves in water to the extent of 0·3735 gram in 100 grams at 25° (*diethyl* ester, colourless, mobile liquid, b. p. 140—143°/10 mm., 262—263°/772 mm., D_4^{20} 1·0145, n_D^{18} 1·45709, $[\alpha]_D^{18}$ −36·18°; *monoethyl* ester, [β-form], colourless, almost odourless, viscous liquid, b. p. 172—175°/10 mm.).

When a faintly alkaline solution of dehydro*iso*fenchoic acid is oxidised by potassium permanganate (1%) at 0°, about two atoms

of oxygen are absorbed, and the syrupy product appears to consist mainly of a *lactonic acid*, which could not be isolated in the pure condition. At ordinary temperatures under the same conditions, oxidation proceeds until rather more than four atoms of oxygen have been used, and the product is a crystalline acid, $C_8H_{10}O_3$ (see later). If, however, a brisk current of carbon dioxide is passed through the mixture during oxidation and an excess of acid is immediately added, *αδ-diketo-ββ-dimethylhexoic acid*,

$$CO_2H\cdot CO\cdot CMe_2\cdot CH_2\cdot COMe,$$

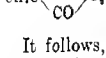
is obtained as a colourless, viscous liquid, which can be neither caused to crystallise nor distilled, even under diminished pressure. It does not appear to react normally with phenylhydrazine or semicarbazide, but its constitution follows from its oxidation by hydrogen peroxide to mesitonic acid. $CO_2H\cdot CMe_2\cdot CH_2\cdot COMe$, m. p. 75° (*semicarbazone*, m. p. 197·5° [decomp.], phenylhydrazone, m. p. 135°). The acid is converted by boiling dilute solutions of alkali hydroxides into the acid, $C_8H_{10}O_3$, which is identical with the substance described by Perkin, Thorpe, and Walker (T., 1901, 79, 729), to which they ascribed the annexed formula. It has m. p. 180° (*semicarbazone*, m. p. 255°, phenylhydrazone, yellow needles, m. p. 222°, *methyl* ester, colourless, moderately mobile liquid, b. p. 112—113°/14 mm., D_4^{20} 1·0783, $n_D^{18\cdot5}$ 1·47860). It is converted by bromine in acetic acid solution into a *dibromo-acid*, $C_8H_{10}O_3Br_2$, shining, rhombic leaflets, m. p. 164°, which, on reduction with zinc dust and acetic acid, yields dimethyl*cyclo*pentanonecarboxylic acid, m. p. 104°, which is also obtained by reduction of the acid, $C_8H_{10}O_3$, itself (compare Perkin, Walker, and Thorpe, *loc. cit.*). When oxidised by permanganate in alkaline solution, it yields *αα-dihydroxy-ββ-dimethylglutaric acid*, m. p. 85° (which, when preserved in a vacuum desiccator, readily passes into *α-keto-ββ-dimethylglutaric acid*, m. p. 99°), and *as*-dimethylsuccinic acid. The author doubts the correctness of the formula ascribed to the acid, $C_8H_{10}O_3$, by Perkin, Walker, and Thorpe, and prefers to regard it as 5:5-dimethyl-Δ^1-*cyclo*penten-3-one-1-carboxylic acid, its oxidation occurring in accordance with the scheme:



H. W.

The Derivation of Valency Laws. The Principle of Cationic Partial Valencies. Hugo Kauffmann (*Ber.*, 1919, 52 [*B*], 1422—1435).—In connexion with the problem of halochromism, it has already been shown that the basic functions of the dye and the colour of its salts do not always run parallel. In the case of some dimethoxy derivatives of triphenylcarbinol, for example, it

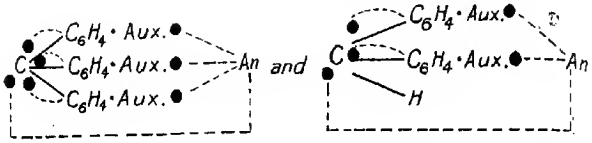
has been found that whereas the 2:4-compounds are more basic than the 3:4-, and these much more so than the 2:5-isomerides, the latter give the deepest coloured salts. That is, resorcinol derivatives give the strongest bases, but quinol derivatives the most deeply coloured salts (A., 1914, i, 39). The principle may be established, therefore, that two auxochromes have the greatest effect on a chromogen when they are in the para-position to each other. This principle has already been tested in the case of benzene derivatives having the auxochrome and chromophore in the same ring (A., 1906, i, 841; 1911, i, 368, 930; 1912, i, 863), but now, in order to throw light on the triphenylcarbinol salts, it has been examined in the case of some compounds in which the chromophore is connected by a carbon chain to the nucleus. The methoxyl group is chosen as the auxochrome, to avoid complications such as quinonoid isomerism and betaine-like salt formation. As the following table shows, the 2:5-isomerides have the deepest shades of colour.

Chromophore.	2:5-.	3:4-.	2:4-.
$CH{:}CH{\cdot}NO_2$	Orange-red	Yellow	Yellow
$CH{:}CMe{\cdot}NO_2$	Orange	Pale yellow	Yellow
$CH{:}CPh{\cdot}NO_2$	Orange	Lemon-yellow	Yellow
$CH{:}CPh{\cdot}CO_2H$	Pale yellow	White	White
$CH{:}CPh{\cdot}CN$	Yellow	White	Pale yellow
$CH{:}C(CN){\cdot}CO_2Et$	Yellow or orange	White	Greenish-yellow
$CH{:}C(CN){\cdot}CN$	Golden-yellow	Pale yellow	Pale yellow
$CH{:}CBz{\cdot}CN$	Yellow or orange	Straw-yellow	Pale yellow
 ...	Brick-red	Chrome-yellow	Lemon-yellow

It follows, therefore, that the salt character of a triphenylcarbinol derivative is governed by one law and its colour by another, quite independent in its operation, and, consequently, a formula for these dyes must be so adduced that it is possible to express in it how variations in colour and salt character can proceed independently. None of the formulæ proposed hitherto satisfy this condition, not even Hantzsch's "conjugation" formula (A., 1919, ii, 254). The author proceeds to develop an electrochemical hypothesis, from the two principles already laid down by him, namely, the law of the decentralisation of chemical functions (A., 1914, i, 40) and the principle of variable states (A., 1916, i, 417).

The valency of a system which is directed towards an anion is termed a "cation valency." This may have its seat in one atom of the system, but is generally divided and the partial valencies distributed over several parts of the molecule. The more the valency is subdivided, the more strongly basic will the system be. Subdivision of valencies is also the cause of colour, and auxochromes are groups which provide cationic partial valencies. In the case of the triphenylmethane compounds, any change in the cationic valency fragments of the auxochrome is accompanied by a similar change at the central carbon atom. That is, the more the auxochrome valency is subdivided the more also will the fourth valency of the central carbon atom be, and these valency fragments will be cationic, for they are opposed to the auxochrome valencies.

In the case of crystal-violet and tetramethyldiaminobenzhydrol the "formulæ of state" may be written thus:



where Aux. = auxochrome, an. = anion, and the heavy points mark the seat of cationic partial valencies. In the first compound the auxochrome and central carbon atom valencies are more scattered than in the second, and it is therefore more basic. It is not much more deeply coloured, however, from which it follows that subdivision of cationic valencies does not cause colour, and the central carbon atom in the triphenylmethane dyes is not the seat of the colour. These dyes have three seats of colour, namely, the ring carbon atoms, which are united to the central carbon atom.

The following new compounds are prepared by the condensation of the dimethoxybenzaldehydes with various agents. *ω-Nitro-3:4-dimethoxy-ω-methylstyrene*, $C_6H_3(OMe)_2\cdot CH{:}CMe\cdot NO_2$, m. p. 73°, and the 2:4-*dimethoxy*-compound, m. p. 79°, from nitroethane under the influence of ethylamine. *β-Nitro-3:4-dimethoxystilbene*, $C_6H_3(OMe)_2\cdot CH{:}CPh\cdot NO_2$, m. p. 109°, and the 2:4-*dimethoxy*-compound, m. p. 120°, from phenylnitromethane. *3:4-Dimethoxy-α-phenylcinnamic acid*, $C_6H_3(OMe)_2\cdot CH{:}CPh\cdot CO_2H$, m. p. 224°, and the 2:4-*dimethoxy*-compound, slender needles, m. p. 191°, from sodium phenylacetate and acetic anhydride. *Ethyl α-cyano-3:4-dimethoxycinnamate*, $C_6H_3(OMe)_2\cdot CH{:}C(CN)\cdot CO_2Et$, m. p. 155°, and the 2:4-*dimethoxy*-compound, m. p. 143°, from ethyl cyanoacetate. *α-Cyano-3:4-dimethoxycinnamonitrile*, $C_6H_3(OMe)_2\cdot CH{:}C(CN)_2$, m. p. 147°, and the 2:4-*dimethoxy*-compound, m. p. 144°, from malononitrile. *Phenyl α-cyano-3:4-dimethoxystyryl ketone*, $C_6H_3(OMe)_2\cdot CH{:}CBz\cdot CN$, slender needles, m. p. 106°, and the 2:4-*dimethoxy*-compound, m. p. 156°, from ω-cyanoacetophenone. *Phenyl α-cyano-3:4-methylenedioxystyryl ketone*, lemon-yellow needles, m. p. 138°, from piperonaldehyde and ω-cyanoacetophenone, and *phenyl α-cyano-4-hydroxy-3-methoxystyryl ketone*, deep yellow crystals, m. p. 143°, from vanillin. J. C. W.

Resolution of Acid Salts of Dibasic Acids [into Normal Salts and Free Acids] in Aqueous Solution. IV. Th Sabalitschka (*Ber.*, 1919, **52**, [*B*], 1776. Compare A., 1917, i, 700; 1919, ii, 282, i, 433).—Phthalic acid is not dehydrated if its ethereal solution is evaporated without a catalyst, but a trace of sulphuric acid is sufficient to cause the production of considerable quantities of the anhydride (compare Dieckmann and Hardt, A., 1919, ii, 326). After extracting a solution of normal potassium phthalate (0·54

gram in 30 c.c.) for twenty hours with ether, the extract was found to require about 1 c.c. of 0·01*N*-potassium hydroxide for neutralisation, and the aqueous solution the same amount of acid.

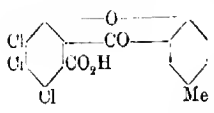
J. C. W.

Condensation of Phthalic Anhydride with Phenols in the Presence of Aluminium Chloride. Fritz Ullmann and Walter Schmidt (*Ber.*, 1919, **52**, [*B*], 2098—2118).—Phenols may be condensed with phthalic anhydride by means of aluminium chloride if acetylene tetrachloride is used as solvent, hydroxybenzoylbenzoic acid derivatives being formed in uniformly good yield. The carbonyl group of the phthalic anhydride attaches itself for the most part to the carbon atom in the *ortho*-position to the hydroxyl group of the phenol. Starting from tetrachlorophthalic anhydride, *o*-hydroxybenzoylbenzoic acid derivatives are almost exclusively obtained, which are readily converted by alkalis into xanthone derivatives.

Phthalic anhydride and *p*-cresol yield 4-*hydroxy*-m-*toluoyl*-o-*benzoic acid*, $OH{\cdot}C_6H_3Me{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$, colourless, prismatic crystals, m. p. 194—195° (corr.), which is converted by sulphuric acid into 1-hydroxy-4-methylanthraquinone, reddish-yellow needles, m. p. 175° (corr.). 3-Hydroxy-*p*-toluoyl-*o*-benzoic acid, prisms, m. p. 211—212° (corr.), and 5-*hydroxy*-o-*toluoyl*-o-*benzoic acid*, colourless, rhombic leaflets, m. p. 219—220°, are similarly obtained from *m*-cresol, and are best separated by fractional crystallisation from nitrobenzene. In the same manner, o-cresol gives a mixture of 2-hydroxy-*m*-toluoyl-*o*-benzoic acid, prisms, m. p. 196—197° (corr.), and 6-*hydroxy*-m-*toluoyl*-o-*benzoic acid*, colourless, rhombic leaflets, m. p. 224—226° (corr.). 2′-*Hydroxy*-o-*benzoylbenzoic acid*, prismatic crystals, m. p. 171—172° (corr.), 4′-*hydroxy*-o-*benzoylbenzoic acid*, rhombic leaflets, m. p. 210° (identified by comparison with the acid obtained by the fission of phenolphthaleinoxime), and small amounts of phenolphthalein are obtained from phenol. 6-*Chloro*-3-*hydroxy*-p-*toluoyl*-o-*benzoic acid*, colourless prisms, m. p. 205—206° (corr.), is prepared from *p*-chloro-*m*-cresol, and is transformed by sulphuric acid monohydrate into 4-*chloro*-1-*hydroxy*-3-*methylanthraquinone*, orange-red needles, m. p. 177° (corr.). The latter is converted by *p*-toluidine in the presence of copper powder into 1-*hydroxy*-4-p-*toluidino*-3-*methylanthraquinone*, bluish-violet needles, m. p. 191° (corr.); the chlorine atom can be replaced by the hydroxyl group by treatment with sulphuric and boric acids at 150—160°, whereby 1 : 4-dihydroxy-2-methylanthraquinone (2-methylquinizarin), carmine-red needles, m. p. 177° (corr.), is formed. It is transformed by nitrous acid in the presence of boric and sulphuric acids into quinizarin-2-carboxylic acid, carmine-red, matted needles, m. p. 249—250° (corr.). 1-*Hydroxy*-4-*toluenesulphonamido*-3-*methylanthraquinone*, yellowish-brown needles, m. p. 213—214° (corr.), is obtained by heating the chlorohydroxymethylanthraquinone with potassium acetate, *p*-toluenesulphonamide, and

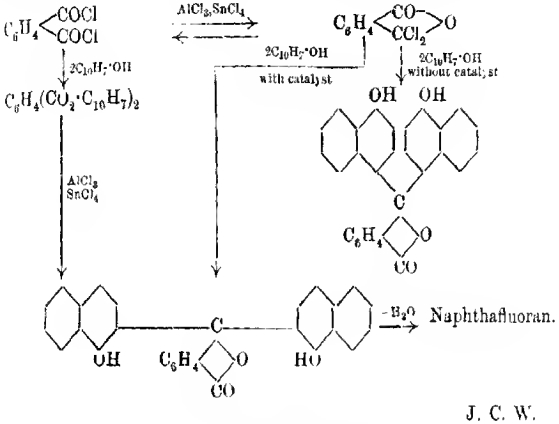
copper acetate in amyl-alcoholic solution, and is hydrolysed to 4-*amino*-1-*hydroxy*-3-*methylanthraquinone*, violet needles, m. p. 257—258° (corr.). Wheu heated with potassium and copper acetates in the presence of naphthalene, the chlorohydroxymethylanthraquinone yields 1-hydroxy-3-methylanthraquinone, m. p. 178° (corr.).

The coudensation of *p*-cresol with tetrachlorophthalic anhydride gives 3:4:5:6-*tetrachloro*-4′-*hydroxy*-m-*toluoyl*-o-*benzoic acid*, m. p. 232—235° (corr.), according to the rate of heating, which is quantitatively transformed by alkali carbonate or hydroxide into 5:6:7-*trichloro*-2-*methylxanthone*-8-*carboxylic acid* (annexed formula), colourless, prismatic needles, m. p. 263—266° (corr.). Under similar conditions, *m*-cresol gives 3:4:5:6-*tetrachloro*-3′-*hydroxy*-p-*toluoyl*-o-*benzoic acid*, pale yellow, prismatic plates, m. p. 226—228° (corr.), which yields 5:6:7-*trichloro*-3-*methylxanthone*-8-*carboxylic acid*, long, colourless, prismatic needles, m. p. 254—256° (corr., decomp.). 3:4:5:6-*Tetrachloro*-2′-*hydroxy*-m-*toluoyl*-o-*benzoic acid*, yellow, rhombic plates, m. p. 222—225° (corr.), and 5:6:7-*trichloro*-4-*methylxanthone*-8-*carboxylic acid*, colourless, prismatic needles, m. p. 270—273° (decomp.), are successively prepared from *o*-cresol. Phenol yields 3:4:5:6-*tetrachloro*-2′-*hydroxy*-o-*benzoylbenzoic acid*, colourless, shining leaflets, m. p. 216—218° (corr.), and 5:6:7-*trichloroxanthone*-8-*carboxylic acid*, colourless, prismatic needles, m. p. 261—264° (corr.), whilst β-naphthol gives 3:4:5:6-*tetrachloro*-2′-*hydroxy*-2-α-*naphthoylbenzoic acid*, yellow, rhombic plates, m. p. 214—217° (corr.), and 4′:5′:6′-*trichloro*-1:2-*naphthaxanthone*-1′-*carboxylic acid*, needles, m. p. 273—275° (corr, decomp.). H. W.



Condensation of Phthalyl Chloride with α-Naphthol. Wilhelm Csányi (*Ber.*, 1919, **52**, [*B*], 1788—1793. Compare Werner, T., 1918, **113**, 20).—The following compounds have been isolated from the product of the condensation of phthalyl chloride with α-naphthol by Sörensen and Palitzsch's method (A., 1910, ii, 446). (1) *α-Naphthyl phthalate*, pale yellow bundles of needles, m. p. 155°, insoluble in sodium hydroxide. (2) An *o*-naphtholphthalein, almost insoluble in cold alcohol, crystallising from the hot solvent in yellowish-red, prismatic needles, m. p. 234—235°; soluble with dark green colour in sodium hydroxide (compare Copisarow and Weizmann, T., 1915, **107**, 878); soluble with ultramarine colour in concentrated sulphuric acid, the solution becoming eosin red with ochre-yellow fluorescence on warming, owing to dehydration to α-naphthafluoran. (3) The *p*-naphtholphthalein, which dissolves in cold alcohol, gives a blue solution in sodium hydroxide, and cannot be condensed to the fluoran. Under the above conditions the yield of the ortho-phthalein is very small, but it is greatly increased if anhydrous aluminium or stannic chloride is present.

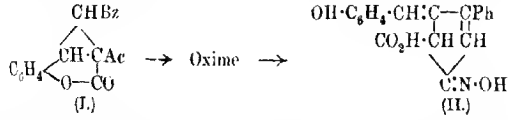
The complete system, α-naphthol–phthalyl chloride, is influenced, therefore, by the tautomerism of phthalyl chloride, the equilibrium of which is displaced in favour of the unsymmetrical form by the metallic chlorides, and also by the effect of these agents on the ester (compare A., 1919, i, 327). The system is reproduced thus:



J. C. W.

A New Group of *cyclo*Propane Derivatives. IV. Derivatives of the 3-Acyl-3 : 4-phenacylidenedihydrocoumarins. Oskar Widman (*Ber.*, 1919, **52**, [*B*], 1652—1662. Compare A., 1918, i, 347, 398).—Some reactions of 3-acetyl- and 3-propionyl-3:4-phenacylidenedihydrocoumarins and phenacylidenecoumarinic esters are described.

3-Acetyl-3:4-phenacylidenedihydrocoumarin (I) forms an *oxime*, quadratic prisms or elongated tablets, m. p. 230° (decomp.), which dissolves in dilute sodium hydroxide on boiling, the yellowish-red solution depositing a *compound*, probably of the formula (II), on acidifying. This product crystallises in small, yellow tablets or prisms, m. p. 184° (decomp.). When treated with semicarbazide



hydrochloride in methyl or ethyl alcohol, alcoholates of the semicarbazone are formed. These lose the alcohol at about 115° in a vacuum, giving the pale yellow *semicarbazone*,

$$C_{19}H_{14}O_3{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

m. p. 204° (decomp.); the *compound* with 1EtOH, crystallises in

long needles which change into small rhombohedra, and the *compound* with 1MeOH forms small, quadratic tablets. In acetic acid solution, however, the product is salicylaldehydesemicarhazone. Similarly, hydrazine hydrochloride produces the azine of salicylaldehyde.

When shaken with sodium ethoxide solution, the 3-acetyl derivative gradually deposits the yellow salt of *α-acetyl-αβ-phenacylidene-dihydrocoumaric acid*, $OH\cdot C_6H_4\cdot\overset{CHBz}{\overset{/\quad\backslash}{CH}}\!\!-\!\!CAc\cdot CO_2H$. The free acid crystallises in colourless, quadratic pyramids, m. p. 177° (decomp.), and slowly reduces permanganate in acetone. The compound also dissolves in boiling 10% sodium hydroxide, depositing a scarlet, flaky salt on cooling, which evolves carbon dioxide and salicylaldehyde (I) on acidifying, thereby changing into *3-keto-1-phenyl-5-salicylidene-Δ¹-cyclopentene*, $CO\!<\!\begin{matrix}CH_2\cdot C{:}CH\cdot C_6H_4\cdot OH\\ |\\ CH{=}CPh\end{matrix}$. This crystallises in nodules of yellow needles, m. p. 202°, readily reduces permanganate, and forms an *acetyl* derivative, pale yellow filaments, m. p. 161°, which yields an *oxime*, pale yellow filaments, m. p. 167° (decomp.), and an *azine*, $[C_{20}H_{16}ON]_2N_2$, reddish-brown filaments, m. p. 232°.

Ethyl α-acetyl-αβ-phenacylidenedihydrocoumarinate dissolves in dilute sodium hydroxide on boiling, and on acidifying the solution deposits *2-hydroxy-4-phenyl-5-α-hydroxy-o-ethoxybenzyl-Δ¹,³-cyclopentadiene-1-carboxylic acid*,

$$OH\cdot C\!<\!\begin{matrix}C(CO_2H)\cdot CH\cdot CH(OH)\cdot C_6H_4\cdot OEt\\ |\\ CH{=}{=}{=}CPh\end{matrix}.$$

This crystallises in large, pale yellow, quadratic prisms, m. p. 164° (decomp.), gives an intense violet coloration with ferric chloride, and forms a *lactone*, glassy, rhombic tablets, m. p. 137—138°, on boiling with acetic anhydride.

3-Propionyl-3:4-phenacylidenedihydrocoumarin reacts with dilute sodium hydroxide to form *3-keto-1-phenyl-5-salicylidene-2-methyl-Δ¹-cyclopentene*, straw-yellow tablets or prisms, m. p. 250°, and ethyl α-propionyl-αβ-phenacylidenedihydrocoumarinate yields *2-hydroxy-4-phenyl-5-α-hydroxy-o-ethoxybenzyl-3-methyl-Δ¹,³-cyclopentadiene-1-carboxylic acid*, stout prisms, m. p. 138°. J. C. W.

Hydroxy- and Dihydroxy-phenylserines and the Parent Substance of Adrenaline. Karl W. Rosenmund and H. Dornsaft (*Ber.*, 1919, **52**, [*B*], 1734—1749).—Erlenmeyer's synthesis of phenylserines from aromatic aldehydes and glycine (A., 1905, i, 131) is of very limited application, but a modification which would admit of the production of phenolic serines would be of considerable interest, because of the relationship between such compounds and adrenaline. Three methods have now been tested, the third being successful, consisting in the condensation of the aldehydes

with ethyl glycine in the presence of sodium. The reaction is represented thus:

(1) $R\cdot CHO + NH_2\cdot CH_2\cdot CO_2Et = R\cdot CH{:}N\cdot CH_2\cdot CO_2Et + H_2O$;
(2) $R\cdot CHO + R\cdot CH{:}N\cdot CH_2\cdot CO_2Et = R\cdot CH(OH)\cdot CH(CO_2Et)\cdot N{:}CHR$

(that is, aldol condensation); (3) hydrolysis to

$$R\cdot CH(OH)\cdot CH(NH_2)\cdot CO_2H + R\cdot CHO.$$

In the case of phenolic aldehydes, the hydroxy-groups are protected by transforming them into ethylcarbonato-groups, which are subsequently removed by treatment with dilute sodium hydroxide in an atmosphere of hydrogen (Fischer's method).

Various views on the development of adrenaline in the body are criticised, and the following scheme is suggested, the precursor being the 3:4-dihydroxyphenylalanine of proteins (Guggenheim, A., 1914. i, 49): ($R = C_6H_3[OH]_2$)

$$R\cdot CH_2\cdot CH(NH_2)\cdot CO_2H \longrightarrow R\cdot CH_2\cdot CH_2\cdot CO_2H \longrightarrow R\cdot CH_2\cdot CO_2H \longrightarrow R\cdot CO\cdot CO_2H$$
$$R\cdot CO\cdot CO_2H + NH_2\cdot CH_2\cdot CO_2H — CO_2 \longrightarrow R\cdot CH(OH)\cdot CH(NH_2)\cdot CO_2H \longrightarrow R\cdot CH(OH)\cdot CH(NHMe)\cdot CO_2H \longrightarrow R\cdot CH(OH)\cdot CH_2\cdot NHMe.$$

It is quite possible that the 3:4-dihydroxyphenylserine itself is a hydrolytic product of protein.

The Unsuccessful Attempts.—Anisaldehyde and ethyl chloroacetate, condensed together by Claisen's method (A., 1905, i, 286), yield *ethyl* p-*methoxyphenylglycidate*, $OMe\cdot C_6H_4\cdot CH\langle{}^{O}_{CH\cdot CO_2Et}$, b. p. 187—191°/18 mm., and the corresponding sodium salt, which reacts with hydroxylamine hydrochloride to give the oxime of *p*-methoxyphenylacetaldehyde and carbon dioxide. Similarly, piperonaldehyde gives *ethyl* 3:4-*methylenedioxyphenylglycidate*, b. p. 205—210°/17 mm., and the sodium salt, which is converted into homopiperonaldoxime. These esters were expected to combine with amines to form serines, but the experiments were unsuccessful. Ethyl carbethoxyglycine, $CO_2Et\cdot NH\cdot CH\cdot CO_2Et$, was expected to combine with benzaldehyde in the presence of sodium to form the *N*-carbethoxy-derivative of the serine, but water is eliminated in the reaction, and the product is a mixture of an *acid* of a new type, $CHPh{:}C(CO_2H)\cdot NH\cdot CO_2H$, silky leaflets, m. p. 187—190° (decomp.), and its *ethyl* ester, needles, m. p. 106—107° (decomp.).

The Successful Experiments.—Ethyl glycine and benzaldehyde are dissolved in ether and mixed with sodium wire. The metal is soon covered with a brown crust of the sodium salt of the phenylbenzylideneserine, $OH\cdot CHPh\cdot CH(CO_2Na)\cdot N{:}CHPh$, which is removed frequently by means of a glass rod. After lifting out any unchanged metal, the sodium salt is dissolved in water and acidified with acetic acid, giving benzaldehyde and phenylserine, m. p. 192° (decomp.). Anisaldehyde behaves in the same way, yielding *p-anisylserine* [*α-amino-β-hydroxy-β-p-methoxyphenylpropionic acid*], white needles, m. p. 185—186°.

p-*Ethylcarbonatobenzaldehyde*, $CO_2Et\cdot O\cdot C_6H_4\cdot CHO$, a pale yellow liquid, b. p. 170—172°/19 mm., m. p. 13°, from *p*-hydroxybenzaldehyde and ethyl chloroformate in the presence of sodium hydroxide, also reacts with glycine ester, but in this case very little sodium salt is produced. The main product is the ester of the arylbenzylideneserine, which remains in the ethereal solution and is hydrolysed and deposited as the *hydrochloride*, m. p. 181°, of the p-*ethylcarbonatophenylserine* ester, long, prismatic needles, m. p. 124°, on adding alcoholic hydrogen chloride. The free ester is obtained from the salt by means of ammonia solution, but the salt may be converted directly into p-*hydroxyphenylserine* [*α-amino-β*:4-*dihydroxy-β-phenylpropionic acid*], small needles or leaflets, decomp. 217°, by shaking it with *N*-sodium hydroxide.

In the case of m-*methoxy*-p-*ethylcarbonatobenzaldehyde*, m. p. 71° (from vanillin), the intermediate sodium salt is deposited in small amount, the ethereal solution only being worked up, as above. *Vanillylserine* [*α-amino-β* : 4-*dihydroxy*-3-*methoxyphenylpropionic acid*] forms slender needles, m. p. 195° (decomp.). Similarly, 3:4-*diethylcarbonatobenzaldehyde*, b. p. 215—217°/13 mm. (from protocatechualdehyde), yields the *hydrochloride* of 3:4-*diethylcarbonatophenylserine* ester,

$$C_6H_3(O\cdot CO_2Et)_2\cdot CH(OH)\cdot CH(CO_2Et)\cdot NH_2,HCl,$$

white druses, m. p. 151—152° (decomp.), and 3:4-*dihydroxyphenylserine* [*α-amino-β*:3:4-*trihydroxyphenylpropionic acid*], m. p. 208—210° (decomp.).

Propaldehyde does not behave at all in the same way, but gives rise to a *compound* of the formula $CH_3\cdot CH_2\cdot CH(NH\cdot CH_2\cdot CO_2H)_2$, which crystallises in microscopic needles, decomp. 250°.

J. C. W.

Process of Manufacturing Benzaldehyde. A. I. Appelbaum (U.S. Pat. 1302273).—Aldehydes are produced from aromatic hydrocarbons by heating with an oxidising agent and a catalyst in the presence of an acid. For example, a mixture of 92 parts of toluene, 100 parts of manganese dioxide, 150 parts of sulphuric acid, and 5 parts of ferric, copper, or cerium sulphate is heated to boiling in a digester, then distilled with steam, and the distillate fractionated to separate benzaldehyde from unchanged toluene.

A New Method for the Conversion of Carboxylic Acids into Aldehydes. Adolf Sonn and Ernst Müller (*Ber.*, 1919, 52, [*B*], 1927—1934).—The replacement of the chlorine atom of iminochlorides by hydrogen is readily effected by the action of stannous chloride in ethereal solution; the tin double salts of the corresponding Schiff's bases appear to be formed as intermediate products, and these pass readily into aldehydes and aniline salts when heated with dilute acids, or, in certain cases, when simply treated with steam. Thus, when a solution of benzanilideiminochloride in dry ether is gradually added to pure stannous chloride dissolved in ether in the presence of dry hydrogen chloride, the *tin* salt, $C_{13}H_{12}NCl_3Sn$, lemon-yellow, crystalline powder, m. p. 165° to a

foaming mass, which becomes completely liquid at 200° (decomp.), gradually separates; it is converted by dilute hydrochloric acid into benzaldehyde, the yield being practically quantitative. Similarly, cinnamaldehyde is prepared in 92% yield from cinnamanilideiminochloride. p-*Ethylcarbonatobenzanilide*,

$$CO_2Et\cdot O\cdot C_6H_4\cdot CO\cdot NHPh,$$

long, colourless needles, m. p. 182° (uncorr.), is transformed into the corresponding *iminochloride*, colourless, unstable needles, m. p. 84°, which yields *p*-hydroxybenzaldehyde, m. p. 115—116°. Similarly, 3:4:5-*trimethoxybenzanilide*, $C_6H_2(OMe)_3\cdot CO\cdot NHPh$, colourless needles, m. p. 141°, gives successively the corresponding *iminochloride*, long, unstable needles, b. p. 222—223°/13 mm., m. p. 106°, and 3:4:5-trimethoxybenzaldehyde, m. p. 74—75°.

Pure stannous chloride appears to be essential for the success of the operations. Commercial grades only dissolve in ether in the presence of a large excess of hydrogen chloride, which renders the solutions unsuitable for the reduction of the more sensitive iminochlorides.

Attempts to convert aliphatic acids into aldehydes by this process have been abortive up to the present. H. W.

The *cyclo*Propane Series. VIII. Nitro*cyclo*propane Derivatives. E. P. Kohler and H. E. Williams (*J. Amer. Chem. Soc.*, 1919, **41**, 1644—1655).—In the hope of being able to isolate some of the intermediate products which could not be examined in the earlier work (A., 1919, i, 582), the authors have turned their attention to another nitro*cyclo*propane derivative, and now describe *p-bromobenzoylphenylnitrocyclopropane*, which they have prepared in three of the four possible stereoisomeric forms.

p-*Bromophenyl γ-nitro-β-phenylpropyl ketone*,

$$NO_2\cdot CH_2\cdot CHPh\cdot CH_2\cdot CO\cdot C_6H_4Br,$$

small needles, m. p. 101—102° (*semicarbazone*, m. p. 168—169° [decomp.]), is prepared, together with the "dimolecular" *product*, $NO_2\cdot CH(CHPh\cdot CH_2\cdot CO\cdot C_6H_4Br)_2$, by the action of sodium nitromethane on α-pheuyl-γ-(*p*-bromophenyl)propenone. When brominated in carbon tetrachloride solution, it yields three p-*bromophenyl α-bromo-γ-nitro-β-phenylpropyl ketones*,

$$NO_2\cdot CH_2\cdot CHPh\cdot CHBr\cdot CO\cdot C_6H_4Br,$$

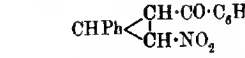
fine needles, m. p. 114·5—115·5°, rhombic tables, m. p. 105—106°, and needles, m. p. 91°, respectively, and a dibromo-*compound*, thin flakes, m. p. 138—139°. Bromination in the α-position to the nitro-group is effected by means of the sodium derivative, whereby p-*bromophenyl γ-bromo-γ-nitro-β-phenylpropyl ketone*,

$$NO_2\cdot CHBr\cdot CHPh\cdot CH_2\cdot CO\cdot C_6H_4Br,$$

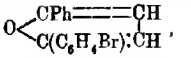
is obtained in needles, m. p. 127°, whilst the corresponding γγ-dibromo-*product* forms thin plates or needles, m. p. about 144—146°. Since it has been previously shown that it is possible to distinguish between bromine compounds in which the bromine is in the α-position to the nitro-group and those in which it is in the α-position relative to the carbonyl by treatment with potassium

iodide, the former undergoing reduction, whilst the latter are transformed into the corresponding iodo-derivatives, the foregoing bromo-derivatives have been boiled with potassium iodide in alcoholic solution; the reaction is found to be a general one, and the following substances are obtained: p-*bromophenyl α-iodo-γ-nitro-β-phenylpropyl ketone*, pale yellow, rhombic plates, m. p. 110°, from the isomerides, m. p. 114·5—115·5° and 105—106° respectively; the nitro-ketone from the γ-monobromo-derivative, and first the γ-monobromo-compound, m. p. 127°, and then the nitro-ketone from the γγ-dibromo-derivative.

3-*Nitro*-2-p-*bromobenzoyl*-1-*phenyl*cyclo*propane*,



m. p. 131°, is obtained by the action of fused potassium acetate on an alcoholic solution of the α-bromo-compound; similar treatment of the γ-bromo-compound leads to the formation of an isomeric *cyclo*propane derivative, fine needles, m. p. 115°, possibly formed as a result of prolonged contact with potassium acetate, since the same substance is formed from the isomeride, m. p. 130°, under similar conditions. A third *isomeride*, needles, m. p. 162—163°, is formed when an alcoholic suspension of either of the other two is treated with very dilute sodium methoxide solution. All three substances give the corresponding open-chain, saturated nitro-ketone, colourless needles, m. p. 101°, when reduced with zinc dust and alcohol. The substance, m. p. 130°, readily combines with hydrochloric acid, giving p-*bromophenyl γ-chloro-β-nitro-γ-phenylpropyl ketone*, $CHPhCl\cdot CH(NO_2)\cdot CH_2\cdot CO\cdot C_6H_4Br$, long, slender needles, m. p. 133°, which on treatment with potassium acetate loses nitrous acid, yielding a mixture of stereoisomeric p-*bromophenyl γ-chloro-γ-phenylallyl ketones*, downy needles, m. p. 179—180°, and yellow plates, m. p. 108—109°, the constitution of which is deduced from the fact that either is converted by permanganate into benzoic and *p*-bromobenzoic acids, and by ozone into *p*-bromobenzoic acid and benzoyl chloride. The hydrochloric acid additive product readily loses hydrogen chloride and nitrous acid when boiled in alcoholic solution, and yields 2-*phenyl*-5-p-*bromophenylfuran*,



colourless or very pale yellow flakes, m. p. 127°. The *cyclo*propane derivatives, m. p.'s 130° and 162° respectively, readily unite with hydrogen bromide, and, according to the manner in which the experiment is conducted, yield two *substances*, $C_{16}H_{13}O_3NBr_2$, colourless needles, m. p. 144° (decomp.), and long needles, m. p. 133°, which are similarly constituted to the hydrogen chloride additive compound, since, like this, they readily pass into the same 2-phenyl-5-*p*-bromophenylfuran. On the other hand, they lose halogen acid more easily than nitrous acid when treated with potassium acetate.

yielding p-*bromophenyl β-nitro-γ-phenylallyl ketone*,

$$CHPh{:}C(NO_2)\cdot CH_2\cdot CO\cdot C_6H_4Br,$$

unstable colourless needles, m. p. 162—163° (decomp.).

The *cyclo*propane derivatives react slowly with bromine when dissolved in boiling carbon tetrachloride and placed in direct sunlight. In this manner, the isomeride, m. p. 130°, yields two isomeric p-*bromophenyl αγ-dibromo-β-phenylpropyl ketones*,

$$C_{16}H_{12}O_3NBr_3,$$

m. p.'s 162—163° and 137° respectively, which can also be prepared by the action of bromine on the γ-bromo-additive product of hydrogen bromide and the *cyclo*propane derivative. (A third *substance*, $C_{16}H_{12}OBr_4$, fine crystalline powder, m. p. 190—193°, which is probably a furan derivative, is also obtained.) When treated with potassium iodide, the bromine additive compounds yield *p-bromophenyl β-nitro-γ-phenylpropenyl ketone*, yellow plates, m. p. 115°, the constitution of which follows from its oxidation to *p*-bromobenzoic and phenylacetic acids.

The action of dilute sodium methoxide solution in converting the *cyclo*propane derivatives of lower m. p. into the isomeride of highest m. p. is somewhat difficult to interpret, but by cautious regulation of the reaction it has been found possible to isolate the methoxy-*compound*, $CH_2Ph\cdot C(OMe){:}CH\cdot CO\cdot C_6H_4Br$, thin needles, m. p. 102—103°, which is a possible intermediate product; the composition of the substance is deduced from its oxidation by permanganate in acetone solution to methyl phenylacetate and *p*-bromobenzoic acid. It is easily hydrolysed by hydrochloric acid to p-*bromobenzoylphenylacetylmethane*,

$$CH_2Ph\cdot CO\cdot CH_2\cdot CO\cdot C_6H_4Br,$$

rhombic plates, m. p. 80—81°, which readily gives a pale green *copper* derivative. H. W.

The *cyclo*Propane Series. IX. Nitro*cyclo*propane Derivatives. Elmer Peter Kohler and M. Srinivasa Rao (*J. Amer. Chem. Soc.*, 1919, **41**, 1697—1704).—The nitro*cyclo*propane derivatives described previously have all contained an aryl group; the authors now describe a similar compound with an alkyl group, and, in order to avoid complications in the preparation, have used *tert.*-valeryl compounds, the substance studied being 3-nitro-2-*tert.*-butyryl-1-phenyl*cyclo*propane, $CHPh\begin{cases}CH\cdot NO_2\\ CH\cdot CO\cdot CMe_3\end{cases}$ which is prepared by the usual methods. The substitution of the *tert.*-butyl- for the phenyl-group does not materially affect the properties of the *cyclo*propane derivative, and, unfortunately, does not lower the boiling points of the substances sufficiently to make distillation under reduced pressure feasible. The new *cyclo*propane readily combines with other substances, and the ring opens in all cases between the carbon atoms attached to the phenyl and trimethylacetyl groups.

γ-*Nitro-β-phenylpropyl* tert.-*butyl ketone*,

$$NO_2\cdot CH_2\cdot CHPh\cdot CH_2\cdot CO\cdot CMe_3,$$

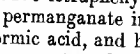
minute, colourless plates, m. p. 74°, is prepared by the action of sodium

methoxide on benzylidenepinacoline and nitromethane. When brominated in carbon tetrachloride solution it yields two isomeric *α-bromo-γ-nitro-β-phenylpropyl* tert.-*butyl ketones*, large needles, m. p. 143—144°, and colourless plates, m. p. 74—75°, the latter of which is readily transformed into the former by boiling with methyl-alcoholic potassium acetate. Both isomerides are slowly converted into 3-*nitro*-2-tert.-*valeryl*-1-*phenyl*cyclo*propane*, cubes, m. p. 94°, by the regulated action of potassium acetate in boiling methyl alcoholic solution. This substance readily loses nitrous acid under the influence of alkalis, and yields *phenylacetyl*-tert.-*valeryl-methane*, $CH_2Ph{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CMe_3$, needles, m. p. 44°, which has also been directly synthesised from ethyl phenylacetate and pinacoline. With phenylcarbimide it yields a *phenylcarbamate*, m. p. 130—132°, and with hydroxylamine it gives 5-*benzyl*-3-tert.-*butyl*iso*oxazole*, m. p. 51°, and 3-*benzyl*-5-tert.-*butyl*iso*oxazole*, m. p. 63°. The nitro*cyclo*propane combines very readily with hydrogen bromide to form *γ-bromo-β-nitro-γ-phenylpropyl* tert.-*butyl ketone*, $CHPhBr{\cdot}CH(NO_2){\cdot}CH_2{\cdot}CO{\cdot}CMe_3$, very unstable crystals, m. p. 66—67°, which readily lose both nitrous acid and hydrogen bromide; with cold potassium acetate, however, chiefly the latter is eliminated with production of *β-nitro-β-benzylidene-ethyl* tert.-*butyl ketone*, $CHPh{:}C(NO_2){\cdot}CH_2{\cdot}CO{\cdot}CMe_3$, long, yellow unstable needles, m. p. 53—54°, in which the double bond must be adjacent to the phenyl group, since benzaldehyde is formed as primary product of its oxidation by permanganate in acetone solution. When the unsaturated nitro-ketone is treated with hydrogen bromide in glacial acetic acid solution, it not only unites with the acid, but also undergoes reduction, yielding 5-*bromobenzyl*-3-tert.-*butyl*iso*oxazole*, needles, m. p. 77—78°, which is reduced by zinc dust and acetic acid to 5-benzyl-3-*tert.*-butyl*iso*oxazole, m. p. 50°.

H. W.

Pyrylium Compounds. V. Enolic and Ketonic Forms of Unsaturated 1 : 5-Diketones. W. Dilthey and Th. Böttler (*Ber.*, 1919, **52**, [*B*], 2040—2054).—The conversion of the condensation product of phenyl styryl ketone and deoxybenzoin into a pyrylium salt has been previously described (A., 1917, i, 578). The *pseudo*-base corresponding with the latter has now been investigated and is shown to be α-hydroxy-ε-keto-αγδε-tetraphenyl-Δ$^{\alpha\gamma}$-pentadiene, $OH{\cdot}CPh{:}CH{\cdot}CPh{:}CPh{\cdot}COPh$; when treated with a moderate amount of alkali, it readily passes into the corresponding diketones. The first case of keto-enolic desmotropy in unsaturated 1:5-diketones is thus presented.

2:3:4:6-*Tetraphenylpyryl ferrichloride*, $C_{29}H_{21}OCl_4Fe$, yellow, shining prisms, m. p. 186°, is prepared by adding hydrated ferric chloride to a warm solution of αε-diketo-αγδε-tetraphenylpentane in acetic acid and acetic anhydride. When warmed with water in the presence of ether, it gives *α-hydroxy-ε-keto-αγδε-tetraphenyl-Δ$^{\alpha\gamma}$-pentadiene*, pale yellow needles, united in clusters, m. p. 112—113°, from which the iron salt is readily re-formed. It does

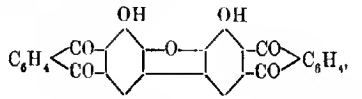
not dissolve in aqueous alkalis, but forms deep violet solutions with alcoholic alkalis. It is rapidly transformed by alcoholic ammonia into 2:3:4:6-tetraphenylpyridine, m. p. 182°. It is rapidly oxidised by permanganate in pyridine solution, yielding benzoic acid, benzoylformic acid, and benzil. Acetylation with acetic anhydride and sodium acetate leads to the formation of *αε-diketo-β-acetyl-αγδε-tetraphenyl-Δ$^{\gamma}$-pentene*, COPh·CHAc·CPh:CPh·COPh, needles, m. p. 172—173°, which gives the ketone, m. p. 142° (*v.c.*), when hydrolysed with alcoholic potassium hydroxide. Attempts to obtain benzoyl- or alkyl-derivatives were unsuccessful. Semicarbazide yields a *mono-semicarbazone*, short, colourless prisms, m. p. 225—226° (decomp.). The enol reacts but slowly with bromine at the ordinary temperature, but, at 30°, the latter is decolourised, and a *substance*, pale yellowish-green prisms, m. p. 166—167°, is formed to which the constitution  is ascribed. The followiug salts of the *pseudo*-base are described: *platinichloride*, $C_{58}H_{42}O_2Cl_4Pt$, orange-yellow leaflets, m. p. 229—230°; *zincochloride*, lemon-yellow leaflets, m. p. 295—296°; *stannichloride*, yellow needles, m. p. 134—135°; *perchlorate*, canary-yellow, shining needles, m. p. 261°; *periodide*, $C_{29}H_{21}OI_3$, brownish ueedles, m. p. 218°; *perbromide*, short, yellow needles, m. p. 217° (also obtained but with greater difficulty from the isomeride, m. p. 142°); *hydrogen bromide*, yellow prisms which when rapidly heated eliminate hydrogen bromide at about 150° and finally melt at 233—235°; *normal bromide*, coarse, orange-red prisms, m. p. 237—238°.

The enolic form is quantitatively converted into *αε-diketo-αγδε-tetraphenyl-Δ$^{\gamma}$-pentene*, COPh·CH$_2$·CPh:CPh·COPh, when its solution of methyl alcohol is geutly warmed with a solution of sodium (1 atom) in the same solvent; it forms colourless, shining needles, m. p. 142—143°, and is less soluble than the enol in all solvents. It is much more stable than the enolic form both towards permanganate and towards bromine; with the latter, however, it slowly yields the same substance, m. p. 166°, which is obtained from the enol. It slowly yields the pyrylium salts which are instantly formed from the enolic variety. Acetylation converts it into the same acetyl derivative as is obtained from the enol. Semicarbazide slowly yields the α-semicarbazone of αε-diketo-αγδε-tetraphenyl-Δ$^{\gamma}$-pentene (see above). [A similar slow reaction is observed with the corresponding saturated diketone, whereby the *α-semicarbazone* of *αε-diketo-αγδε-tetraphenylpentane*, m. p. 238—239°, is produced.] The ketonic is converted into the enolic form by the action of an excess of alcoholic potassium hydroxide. H. W.

Preparation of Benzoquinone. John M. Weiss and Charles R. Downs (U.S. Pat. 1318631).—Benzoquinone is produced by subjecting benzene in the vapour phase to the action of a gas containing oxygen at a suitable temperature and in the presence of a catalyst. G. F. M.

Reduction of Dihydroxythymoquinone by means of Palladium Hydrogen. NELLIE A. WAKEMAN (*J. Amer. Chem. Soc.*, 1919, **41**, 1873—1875).—Thymoquinone is very readily reduced by hydrogen in alcoholic solution in the presence of palladium chloride with the formation of hydrothymoquinone. Similar attempts to reduce dihydroxythymoquinone in alcoholic or ethereal solution were only partly successful, since, although reduction occurred very readily and the solutions became decolorised, the product reverted so easily to the red dihydroxythymoquinone that its isolation in the pure condition was impossible. By performing the experiment in acetic anhydride solution, however, it was found that reduction occurs with less rapidity, but gives an almost quantitative yield of the desired *tetra-acetyl* derivative, colourless, prismatic crystals, m. p. 180—182°, which is stable in air and, on hydrolysis, yields dihydroxythymoquinone in practically quantitative amount. The palladium chloride appears to suffer no loss of activating power when used repeatedly in these experiments. H. W.

Action of Potassium Hypochlorite on Alizarin in Alkaline Solution. R. SCHOLL [with EMIL SCHWINGER and ALB. KABATSCHNIK] (*Ber.*, 1919, **52**, [*B*], 1829—1836. Compare A., 1919, i, 25, 406).—Whereas alkaline ferricyanide solutions cause rupture of the hydroxylated ring of alizarin, the oxidative activity of hypochlorites is manifested in the production of dianthraquinonyl derivatives. The oxidation may be performed by adding potassium hypochlorite solution to a solution of alizarin in potassium hydroxide, or by dissolving the substance in 8% potassium hydroxide and passing in chlorine. The chief product separates as a bluish-black *potassium* salt which is decomposed by dilute sulphuric acid and the acid purified by boiling with nitrobenzene. The product, 3:4:3′:4′-*tetrahydroxy*-2:2′-*dianthraquinonyl*, $C_{28}H_{14}O_8$, forms dark yellowish-red, microscopic, rhombic or hexagonal, prismatic tablets, m. p. 384—395°, and its *sodium* salt is dark blue. It has no affinity for un-mordanted fibres, and is much poorer as a mordant dye than alizarin. The *tetra-acetate* forms yellow crystals, m. p. 278—280°. When distilled with zinc dust in an atmosphere of hydrogen, under 15—30 mm. pressure, it yields 2:2′-*dianthryl*, $C_{28}H_{18}$, yellow, rhombic leaflets, with green fluorescence, m. p. 355°, which is also formed when 2:2′-dianthraquinonyl (A., 1911, i, 453) is treated in the same way. 1:1′-Dianthraquinonyl, however, does not yield the unknown 1:1′-dianthryl under these conditions, but rather *meso*-naphthadianthrone (A., 1910, i, 494). When heated with zinc chloride, the tetrahydroxydianthraquinonyl gives 4:4′-*dihydroxy*-2:2′-*dianthraquinonylene*-3:3′-*oxide*,



which crystallises in yellow needles, m. p. 390—400° (decomp.).
J. C. W.

Synthesis of some Homologues of the Terpenes: Derivatives of 1 : 4-Di*iso*propyl*cyclo*hexane. Marston Taylor Bogert and Clarence Peavy Harris (*J. Amer. Chem. Soc.*, 1919, **41**, 1676—1690).—The peculiar properties of the terpenes appear to be generally associated with the presence of an *iso*propyl and a methyl group, and seem to be due to the former rather than the latter; whilst numerous derivatives having one such group have been investigated, little is known of the effect of two of these groups. The authors have therefore investigated a series of homologues of *p*-di*iso*propylbenzene, which are prepared by the action of magnesium methyl iodide on the methyl ester of terephthalic and partially hydrogenated terephthalic acids and subsequent elimination of water if necessary.

p-*Dihydroxy*iso*propylbenzene*, $C_6H_4(CMe_2\cdot OH)_2$, colourless, short, lustreless needles, m. p. 142·4—142·9° (corr.), is obtained from magnesium methyl iodide and methyl terephthalate (the method of achieving the regulated addition of the reagent to the ester, which is only sparingly soluble in ether, is fully described in the original); when distilled with potassium hydrogen sulphate under diminished pressure, it yields 1 : 4-*di*iso*propenylbenzene*, micaceous plates, m. p. 63·6—64° (corr.), which readily unites with four atoms of bromine without evolution of hydrogen bromide (the *tetrabromide* could not be isolated in the pure condition). Similarly, methyl $\Delta^{1,4}$-dihydroterephthalate, m. p. 128·4—129·4° (corr.), yields 1 : 4-*di*iso*propenyl*-$\Delta^{1,4}$-cyclo*hexadiene*, plates, m. p. 117—117·5° (corr.), the dicarbinol formed as an intermediate product eliminating water spontaneously. The substance adds four atoms of bromine, but hydrogen bromide is readily evolved; however, by suitable adjustment of conditions, a small quantity of the *tetrabromide*, cubic crystals, m. p. 107—109° (corr.), was isolated.

The main product of the action of the Grignard reagent on methyl Δ^1-tetrahydroterephthalate, b. p. 153·3—154·5° (corr.)/20 mm., m. p. 35·2—36·2° (corr.), appears to be the corresponding dicarbinol which, however, could not be isolated in the pure condition. The crude product was therefore dehydrated with potassium hydrogen sulphate, whereby two isomeric *hydrocarbons*, $C_{12}H_{18}$, b. p.'s 95—98°/20 mm. and 105—108° 20 mm. respectively, were produced. Both are colourless oils, which become viscous and slightly yellow on prolonged exposure to air. Both absorb bromine quickly at the outset, but evolution of hydrogen bromide soon begins, so that no pure bromine derivatives could be separated.

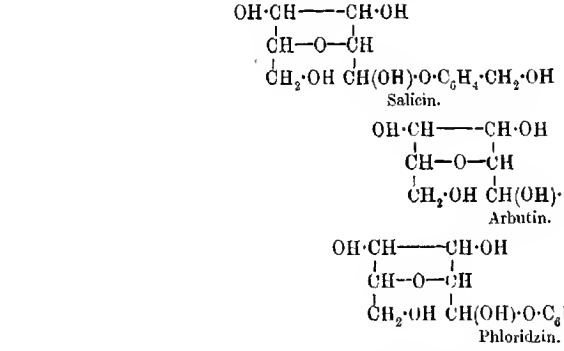
The densities, refractive indices, and magnetic rotatory powers of the new hydrocarbons in the pure state and in a number of solvents have been determined, and the data are discussed with reference to their bearing on the structures assigned to these compounds.

H. W.

Constituents of Resins. Degradation of *d*-Sumaresinolic Acid. Alois Zinke (*Monatsh.*, 1919, **40**, 277—280).—When *d*-sumaresinolic acid is oxidised by chromic acid in glacial acetic acid solution, a monocarboxylic *acid*, $C_{27}H_{40}O_4$, is obtained, which is

isomeric with the acid obtained from *d*-siaresinolic acid (A., 1919, i, 129); it is best purified by crystallisation from benzene, from which it separates in coarse prisms $+C_6H_6$, the solvent being only completely expelled at 150° in a vacuum. The pure substance has m. p. 260—261°. The *barium* salt is described. When thus oxidised, *d*-sumaresinolic acid loses three carbon and eight hydrogen atoms; hence it probably contains a propyl or *iso*propyl group, and its formula may be written $C_{26}H_{10}O_2(C_3H_7)\cdot CO_2H$. H. W.

The Distillation of certain Glucosides under Reduced Pressure. Amé Pictet and Henry Goudet (*Helv. Chim. Acta*, 1919, **2**, 698—703).—The fact that the majority of the naturally occurring glucosides are lævorotatory, although yielding dextrose on hydrolysis, has led the authors to doubt whether they are in reality derivatives of the latter substance. To throw light on the question, they have distilled salicin, arbutin, and phloridzin under reduced pressure, and, in each case, have isolated lævoglucosan (compare Tanret, A., 1894, i, 564; Pictet and Şarasin, A., 1918, i, 59) from among the products of distillation. They are therefore led to suggest the annexed formulæ for the glucosides:



Salicin.

Arbutin.

Phloridzin.

Hydrolysis of the glucosides by barium hydroxide solution yields primarily an unstable hydrate (annexed formula), which passes into lævoglucosan by loss of water. With acids, the rupture of the ring also occurs with formation of dextrose.

Salicin, on distillation, yielded an aqueous liquid containing a little furfuraldehyde, and a pasty mass from which lævoglucosan, m. p. 179—180°, $[\alpha]_D^{20}$ −66·73° in aqueous solution, was isolated. Arbutin gave an aqueous liquid containing acetic acid and furfuraldehyde, and a pasty mass from which lævoglucosan and quinol were obtained, whilst phloretic acid, phloroglucinol, and lævoglucosan were isolated from the semi-solid product from phloridzin. H. W.

Chemistry and Pharmacology of Aloes. I. Products of the Oxidation of the Constituents of Aloes by means of Alkali Persulphate. EUGEN SEEL (*Arch. Pharm.*, 1919, **257**, 212—228. Compare A., 1901, *i*, 92; 1917, i, 41, 577).—The constituents of aloes of pharmacological importance are: (1) Aloin, which is crystalline and soluble in water; (2) aloëtin, which is amorphous and soluble in water; (3) resin or crude resin, which is amorphous and insoluble in water in the cold; (4) emodin, which occurs to the extent of less than 1%, and is very sparingly soluble even in hot water. The products obtained when the first three of these components are oxidised with potassium or ammonium persulphate have been studied.

In the case of aloin, the oxidation proceeds most simply and smoothly in very dilute aqueous solution, a series of colour changes taking place. According as the reaction is slow or rapid, it yields puraloin I either alone or mixed with puraloin II. These two products form red or browuish-red, amorphous powders, and have not been obtained quite free from ash. The results of analyses and molecular weight determinations of their derivatives indicate the formulæ, $C_{12}H_{10}O_6$ for puraloin I, and $C_{13}H_{12}O_6$ for puraloin II. Both are partly hydrated, and they dissolve in alkalis or concentrated acids, giving faintly violet-red or reddish-brown colorations; they are not resolved by acids, but are converted to a greater or less extent into a black powder, termed puralonigrin, owing to its analogy to alonigrin. The formulæ indicate the absence from the puraloins of an anthraquinone nucleus, and puraloin I is regarded as a dihydroxymethyldihydronaphthaquinonecarboxylic acid, and puraloin II as a dihydroxymethyldihydronaphthaquinoneacetic acid. Quantitative study of the oxidation of aloin by persulphate indicates that the sugar-residue of the glucoside is oxidised to carbon dioxide, aud that part of the anthraquinone ring also undergoes attack. Since the oxidation products are insoluble in water and dilute acid, and are thus precipitated and protected from further oxidatiou, the reaction lends itself to the quantitative evaluation of aloes.

Oxidation of aloin by persulphate in alkaline solution yields products which are more untractable than the puraloins, and have not been investigated in detail.

Puraloin I, which is insoluble in 96% alcohol, blackens at 230—240°, and sinters and decomposes at about 340—350°. *Puraloin II* differs from puraloin I principally in its solubility in 96% alcohol. Both are capable of acetylation, the products being non-crystalline and possessed of a marked tendency to form colloidal solutions. *Triacetylpuraloin I*, $C_{12}H_7O_6Ac_3$, is yellowish-brown, and sinters and turns brown at 180—190°. *Diacetylpuraloin II* (?), $C_{13}H_{10}O_6Ac_2$, is brown, aud remains unchanged at 300°. On benzoylation, puraloin I yields a reddish-yellow powder which is intermediate in composition between the di- and tribenzoyl derivatives, and gradually decomposes and blackens at above 200°. *Dibenzoylpuraloin II*, $C_{13}H_{10}O_6Bz_2$, forms a reddish-yellow

powder, and sinters at 220° and carbonises at a higher temperature. Both puraloins yield ochre-yellow *monobromo*-derivatives, $C_{12}H_9O_6Br$ and $C_{13}H_{11}O_6Br$ respectively, which gradually darken at above 200°.

The action of persulphate on aloëtin yields principally puraloins I and II, but the proportions of secondary products are greater than those obtained from aloin. Oxidation of the crude resin also yields the two puraloins.

When administered in single doses of 0·5—2·0 grams, the puraloins exert a mild laxative action, which occasionally fails, but is most trustworthy with children and dogs. T. H. P.

Chemistry and Pharmacology of Aloes. II. Products of the Oxidation of the Constituents of Aloes by Caro's Acid. Eugen Seel (*Arch. Pharm.*, 1919, **257**, 229—254. Compare A., 1901, i, 92; 1917, i, 577, and preceding abstract).—Of the products obtained by oxidising aloin by means of Caro's acid, the following have been identified: (1) A small proportion of trihydroxymethylanthraquinone, m. p. 223—224°, already known. (2) Two isomeric tetrahydroxymethylanthraquinones, m. p. 185—190° and 232—234° respectively, not previously described in the literature. (3) Numerous hydrogenated tri- and tetra-hydroxymethylanthraquinones, which form products intermediate to aloin and the anthraquinone derivatives, but are not obtained in sufficient quantities to admit of isolation. (4) Three naphthalene derivatives, the compositions of which have not been determined. (5) A compound which was isolated in the form of its bromo-derivative, and may be a derivative of either anthracene or naphthalene.

Tetrahydroxymethylanthraquinone, $C_{15}H_{10}O_6$, forms red crystals, m. p. 185—190°, and its *isomeride*, red crystals, m. p. 232—234°. Acetylation of these compounds yields mostly tarry masses, from which only a small proportion of *tetra-acetyl* derivative, $C_{15}H_6O_6Ac_4$, is obtainable as a bright yellow, crystalline powder, m. p. 196—198°; this acetyl derivative dissolves in concentrated sulphuric acid to a violet solution, and on hydrolysis yields the tetrahydroxymethylanthraquinone, m. p. 232—234°. Benzoylation of the two compounds gives (1) a tetrabenzoyl derivative, $C_{15}H_6O_6Bz_4$, which forms a pale ochre-yellow, microcrystalline powder, m. p. 236—238°, dissolves in concentrated sulphuric acid to a violet-red solution, and on hydrolysis yields the tetrahydroxymethylanthraquinone, m. p. 232—234°; (2) a *compound*, m. p. 225—226°, which differs appreciably in composition from the tetrabenzoyl derivative, and on hydrolysis gives only the tetrahydroxymethylanthraquinone, m. p. 232—234°, although it is obtained from the isomeride with m. p. 185—190°. Whether the latter is isomeric with the compound, m. p. 232—234°, or merely an impure form of it, is still uncertain.

After complete extraction of the oxidation products of aloin with chloroform or ether, extraction with 90—96% alcohol removes a compound which blackens slowly at above 240° and agrees approximately in composition with puraloin I, although in solu-

bility in strong alcohol it corresponds with puraloin II. This compound yields an *acetyl* derivative, $C_{12}H_5O_6Ac_3$ or $C_{12}H_7O_6Ac_3$, which forms yellowish-white flocks, m. p. 115—120°, and a *tribenzoyl* derivative, $C_{12}H_5O_6Bz_3$ or $C_{12}H_7O_6Bz_3$, which sinters at 220° and melts and decomposes at 240°. A compound of similar composition to that soluble in strong alcohol may afterwards be extracted from the oxidation products by means of dilute alcohol.

The action of Caro's acid on aloëtin yields: (1) Trihydroxymethylanthraquinone, m. p. 223—224°. (2) A tetrahydroxymethylanthraquinone agreeing in properties with the compound, m. p. 232—234°, but having m. p. 215°. (3) A compound, $C_{15}H_{10}O_6$, which has no sharp melting point, and yields a diacetyl derivative, apparently with simultaneous loss of water, and a dibenzoyl derivative, $C_{15}H_8O_6Bz_2$, showing incipient fusion at 225° and carbonisation at a higher temperature. (4) A small proportion of a dark brown powder which does not melt sharply, but blackens at a high temperature, and has approximately the composition of puraloin I. (5) A compound separable as its bromo-derivative, which darkens at 180°, but does not melt at 290°, and has the properties, but not the composition, of the bromo-derivative similarly obtained from the oxidation products of aloin.

The products obtained when the resin is oxidised by means of Caro's acid indicate that this resin consists mostly of resinified aloëtin, together with a little resinified aloin.

Oxidation of emodin by Caro's acid yielded no well-defined products, but the results obtained show that emodin is not readily converted into a tetrahydroxymethylanthraquinone in this way.

Trihydroxymethylanthraquinone or emodin acts as a mild purgative, without secondary effects, when administered to man and animals in doses of 0·2—0·4 gram at intervals of three hours, whereas smaller doses often produce such secondary effects and are sometimes without purgative action. Tetrahydroxymethylanthraquinone or hydroxyemodin has a weaker purgative effect than emodin, doses of 0·5 gram being often necessary; like emodin, it may be administered subcutaneously. T. H. P.

Chemistry and Pharmacology of Aloes. III. Products of the Oxidation of the Constituents of Aloes by Hydrated Sodium Peroxide. Eugen Seel (*Arch. Pharm.*, 1919, **257**, 254—259).—Oxidation of aloin by means of sodium peroxide yields emodin and a residue which, when treated with bromine, gives a crystalline *dibromo*-derivative, darkening at about 145°, m. p. 160—162° (decomp.), corresponding in composition with a dibromide of puraloin I, $C_{12}H_4O_6Br_2$. Thus, by sodium peroxide in alkaline solution, aloin is only partly resolved into emodin, the greater part of the molecule, including the sugar residue, being attacked only by persulphate. These results confirm the glucosidic character of aloin (compare Léger, A., 1904, i, 907).

The action of sodium peroxide on aloëtin is similar to that on aloin, the yield of emodin being very small; with the crude resin,

also, only small proportions of emodin are obtained. Emodin itself is not oxidised further by sodium peroxide, but may be partly purified, only the anthraquinone derivative remaining unaltered.

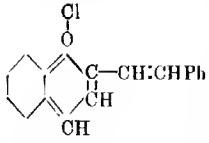
T. H. P.

Anemonin. III. Constitution of Anemolic Acid. Y. Asahina and A. Fujita (*Yakugaku Zasshi* [*J. Pharm. Soc. Japan*], 1919, **448**, 471—484).—Anemonin suspended in methyl alcohol and reduced with 3% sodium amalgam and glacial acetic acid at 5° gave *dihydroanemonin*, $C_{10}H_{10}O_4$, m. p. 172°, in 80—90% yield, which exhibits a normal molecular weight in freezing phenol. It is easily transformed by heating with hydrochloric acid into *anemolic acid*, $C_{10}H_{14}O_6$, which yields a *disemicarbazone*, $C_{12}H_{20}O_8N_8$, m. p. 158°. When the acid is dissolved in ammonia, it gives a precipitate, $C_{10}H_{16}O_4N_2$, which has m. p. 195° after recrystallisation from hot water, gives the pine-shaving reaction, and with hydrochloric acid yields pyrrole-2:5-dipropionic acid, m. p. 170°. From these facts, the authors conclude that anemolic acid is identical with dilævulinic acid, a conclusion confirmed by comparison with the substances synthesised by Kehrer and Hofacker's method (A., 1897, i, 214). On the other hand, sebacic acid, m. p. 131°, is obtained when dihydroanemonin is reduced with platinum black and hydrogen. So far as is known, dihydroanemonin ought to have a constitution similar to that of angelicolactone. Dihydroanemonin when boiled with anisaldehyde and aniline yields a light yellow condensation product, $C_{26}H_{22}O_6$, m. p. 200°. Chemical Abstracts.

The Tinctorial Properties of some Anthocyanins and certain Related Compounds. I. Arthur E. Everest and Archibald J. Hall (*J. Soc. Dyers*, 1919, **35**, 275—279).—The authors record dyeing tests of various anthocyanins and anthocyanidins, and of the colouring matters of the viola, rose, lupin, pelargonium, sweet pea, bilberry, black currant, cranberry, and radish.

An improved process is given for the preparation of 2-*o*-hydroxystyrylbenzopyrylium chloride, which the authors find to have the formula $C_{17}H_{13}O_2Cl.2H_2O$ (compare Decker and Felser, A., 1908, i, 906, who give $1H_2O$).

When salicylaldehyde is condensed with styryl methyl ketone, yellow crystals of a *substance*, possibly of the annexed formula, are obtained, but could not be satisfactorily analysed. Contrary to the statement of Harries and Busse (A., 1896, i, 301), *o*-hydroxybenzylidenediacetophenone (Bablich and Kostanecki, A., 1896, i, 239; Cornelson and Kostanecki, A., 1896, i, 240) is produced by condensing acetophenone and salicylaldehyde by means of 10% sodium carbonate solution.



J. C. C.

Experimental Studies on Plant Pigments. B. Harrow and W. J. Gies (*Proc. Soc. Expt. Biol. Med.*, 1918, **16**, 8—10).—Observations are reported on (*a*) flavones, a group of yellow pig-

ments characterised by the production, in their solutions, of intense yellowish-brown colour on the addition of aqueous ammonia, and of (*b*) anthocyanins, a group of red, violet, or blue pigments, which in solution change to bluish-green on the addition of acid. These pigments were obtained from tulips. Active (nascent) hydrogen reduces flavone to anthocyanin. The latter can be further reduced to a leuco-base, which in turn, by exposure to air, or more rapidly by addition of an oxidising agent, is reconverted into anthocyanin. Anthocyanin, isolated in a fairly pure condition by Willstätter's method, has been oxidised to flavone with the aid of hydrogen peroxide. Flavone thus obtained from anthocyanin can be reduced again to anthocyanin. Anthocyanin when extracted with alcohol made anhydrous with copper sulphate yields a red extract, whereas if the extraction is made with alcohol rendered anhydrous with calcium oxide, a green solution is obtained. Anthocyanin, prepared according to Willstätter's method and dissolved in absolute alcohol, was compared with phenolphthalein, and found to be its equal in point of delicacy. It is superior in that a change from alkali to acid is indicated by a sharp change from green to red, and not from red to no colour at all. CHEMICAL ABSTRACTS.

Furyl Alkyl Ketones. K. MONOYA (*J. Pharm. Soc., Japan*, 1919, **447**, 357—401).—The relation between the constitution of furyl alkyl ketones and their optical properties, and also their action with sodium and alkyl nitrite, have been investigated. The ketones were prepared from furancarboxylonitrile (pyromuconitrile) and magnesium alkyl haloids in dry ether, the intermediate products being decomposed by heating with sulphuric acid and a little oxalic acid. Thus were prepared *furyl benzyl ketone*, plates, m. p. 47—48° (*oxime*, m. p. 125—126°; *semicarbazone*, m. p. 171—172°), furyl methyl ketone, $D_4^{23\cdot3}$ 1·0977, n_D 1·50177, furyl ethyl ketone, $D_4^{23\cdot5}$ 1·0587, n_D 1·49623, furyl propyl ketone, D_4^{14} 1·0416, n_D 1·49970, furyl *iso*butyl ketone, $D_4^{14\cdot6}$ 1·0160, n_D 1·49488, and furyl *iso*amyl ketone, D_4^{14} 0·9988, n_D 1·49260. The exaltation of the molecular refraction of the ketones increases with the molecular weight. During the preparation of the last two ketones, *ketimines* were isolated in the form of double *compounds* with ammonium chloride, $2C_4H_3O\cdot C(:NH)\cdot C_4H_9,NH_4Cl$, m. p. 285—291°, and $2C_4H_3O\cdot C(:NH)\cdot C_5H_{11},NH_4Cl$, m. p. 268—270°. Since these are easily converted into the ketones by treatment with hydrochloric acid, the formation of the latter is represented by the scheme:

$$C_4H_3O\cdot CN + MgRX \longrightarrow C_4H_3O\cdot CR:N\cdot MgX \longrightarrow C_4H_3O\cdot CR:NH \longrightarrow C_4H_3O\cdot COR.$$

Ethyl pyromucate, pyromucic acid, β-benzaldoxime, and oximinodeoxybenzofuroin are formed when furyl benzyl ketone is treated with ethyl nitrite and sodium in dry ether at −13°; the products are isolated by neutralising the mixture with 1% sodium hydroxide, extracting with ether, saturating the aqueous solution with carbon

dioxide, and then acidifying it with hydrochloric acid. The course of the decomposition is represented thus:

$$C_4H_3O\cdot CO\cdot CH_2Ph + OEt\cdot NO = C_4H_3O\cdot CO\cdot CHPh\cdot NO + EtOH$$

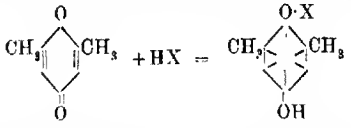
$$C_4H_3O\cdot CO\cdot CPh{:}N\cdot OH \quad C_4H_3O\cdot CO_2Et + CH_2Ph\cdot NO[\longrightarrow CHPh{:}N\cdot OH]$$

Furyl amyl ketone yields valeraldoxime, and the other ketones yield similar products when treated in this manner. By treatment with sodium and amyl nitrite, menthone yields γ-keto-βζ-dimethyloctoic acid (semicarbazone, m. p. 151—152°).

CHEMICAL ABSTRACTS.

Optical Chemical Notes on the Oxonium Salts of Pyrones and Thiopyrones. A. HANTZSCH (*Ber.*, 1919, **52**, [*B*], 1535—1544).—The absorption curves of a number of pyroxonium salts are discussed.

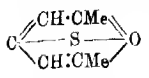
2:6-Dimethyl-1:4-pyrone shows the rudiments of an absorption band at about $1/\lambda = 3600$ in concentrated alcoholic solutions, that is, in the region of the acetone band. This ketone band disappears when the pyrone is dissolved in concentrated sulphuric acid, the curves corresponding closely with those given by pyridinium salts. This is in accordance with Baeyer's formula for the pyroxonium salts (A., 1910, i. 763), the salt formation being represented thus:



Strange to say, the salts of 2:4:6-trimethylpyroxonium have a much greater absorptive power than those of the 4-methoxy-2:6-dimethyl series, that is, the methoxy-group is hypsochromic, and not an auxochrome, in this series. This still further emphasises the analogy between pyroxonium salts and pyridinium salts, for methoxylutidine salts are less absorptive than collidine salts (Purvis, T., 1909, **95**, 295; Baker and Baly, T., 1901, **91**, 1130).

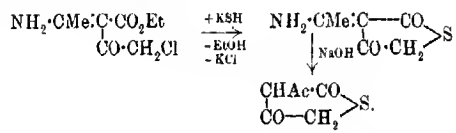
2:6-*Dimethyl*-1:4-*thiopyrone*, $SC<\begin{matrix}CH{:}CMe\\CH{:}CMe\end{matrix}>O$, yellow needles, m. p. 145°, is obtained by the action of phosphorus pentasulphide on the corresponding pyrone in benzene. This forms colourless salts with the strong acids, but they are very easily hydrolysed. That the salts contain a free thiol group is shown by the fact that methyl sulphate gives a salt which may be transformed into 2:4:6-*trimethylpyrthionium perchlorate* (annexed formula). The solutions of the thiopyrone in alcohol, water, or chloroform are yellow, but are cherry-red in ether or light petroleum and have different absorption bands. The highly coloured

solutions may possibly contain an isomeride of the annexed formula. The salts have much weaker absorption in concentrated sulphuric acid, and the effect of replacing the ·SH group by the ·SMe group is to displace the bands towards the red. This is remarkable, for the analogous change in the pyrone series, ·OH to ·OMe, is not accompanied by any optical effect.

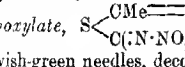


The paper concludes with a criticism of the tendency to formulate all manner of compounds as oxonium salts, for example, the additive compounds of ether with halogen acids, hydroferrocyanic acid, heteropoly-acids, trichloroacetic acid, and even other indifferent substances. J. C. W.

Synthesis of Thiophen Derivatives from Ethyl β-Amino-crotonate. II. ERICH BENARY and L. SILBERSTROM (*Ber.*, 1919, **52**, [*B*], 1605—1613. Compare A., 1915, i, 576).—For some unknown reason, a new supply of 33% potassium hydrosulphide solution has produced from ethyl β-amino-α-chloroacetylcrotonate a compound different to that originally described. The product is apparently *α-acetylthiotetronamide*, for it may be hydrolysed by sodium hydroxide to α-acetylthiotetronic acid (A., 1913, i, 892). It crystallises in long, pale yellow needles, m. p. 233°. The relationships are represented thus:

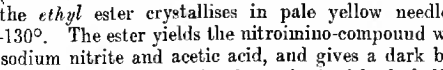


The original product, ethyl 4-hydroxy-2-methylthiophen-3-carboxylate, is always formed if the crotonate is shaken with a suspension of solid potassium hydrosulphide in alcohol. Some further reactions of the ester are now described.

When treated with sodium nitrite in glacial acetic acid, the ester yields *ethyl 3-keto-2-nitroimino-5-methyl-2:3-dihydrothiophen-4-carboxylate*,  , which separates in long, yellowish-green needles, decomp. 211°. This behaves as an acid, for it reddens litmus, forms an orange-coloured *compound* with ammonia, $C_8H_8O_5N_2S,NH_3$, which dissolves in water, and gives precipitates of a red *lead* salt, PbX, and a brownish-red *silver* salt, Ag_2X, and also yields a reddish-brown *potassium* salt, K_2X, and a *di-p-nitrobenzoyl* derivative, greyish-green tablets, m. p. 162°. The corresponding *3-keto-2-nitroimino-5-methyl-2:3-dihydrothiophen-4-carboxylic acid*, made in the same way from the acid (*loc. cit.*), is a brown powder, decomp. above 100°, which forms a *potassium* salt, K_2X, and an explosive *lead* salt, $(C_6H_3O_6N_2S)_2Pb_3$.

With amyl nitrite, however, the products are the normal oximes.

3-*Keto*-2-*oximino*-5-*methyl*-2 : 3-*dihydrothiophen*-4-*carboxylic acid*, , forms green crystals, decomp. 120—130°, and the *ethyl* ester crystallises in pale yellow needles, decomp. 110—130°. The ester yields the nitroimino-compound when treated with sodium nitrite and acetic acid, and gives a dark brownish-red precipitate of a potassium salt when mixed with alcoholic potassium hydroxide. This salt has the colour of permanganate in aqueous solutions, and gives a bright red substance on the addition of acids. The ester also forms a *phenylhydrazone* (*A*), long, white needles, m. p. 152—153°, which is transformed into a pale pink *isomeride*, m. p. 201°, when treated with sodium nitrite and acetic acid, and is converted into *ethyl* 5-*cyano*-1-*phenyl*-3-*methylpyrazole*-4-*carboxylate* (*B*), white needles, m. p. 88—89°, when boiled with alcohol containing a few drops of hydrochloric acid.



(*A*.) (*B*.)

The ester (*B*) is hydrolysed by boiling alcoholic potassium hydroxide to the corresponding *acid*, soft, felted needles, m. p. 250—251° (*silver* salt), which yields the known 1-phenyl-3-methylpyrazole-4 : 5-dicarboxylic acid (Bülow, A., 1900, i, 56) when boiled with 6% aqueous sodium hydroxide. J. C. W.

The Chemical Constituents of the Bituminous Tar Oils Rich in Sulphur (Ichthyol Oils). III. Helmuth Scheibler (*Ber.*, 1919, **52**, [*B*], 1903—1910. Compare A., 1916, i, 65; 1917, i, 153).—The purification of an ichthyol oil is effected in three stages. First, it is heated with soda-lime at 170—180° for some hours, the residue from the distillation being decanted, washed with water, and added to the distillate, the whole being then washed with dilute sulphuric acid and dried. By this treatment, the oil loses its obnoxious odour and becomes paler and more mobile. The dry oil is then heated with sodium, a current of ammonia being admitted, and after this treatment it is mixed with magnesium methyl chloride to destroy the small amount of ketone present. A specimen of crude oil from the south of France (500 grams) gave a pleasant-smelling oil (225 grams) containing only carbon, hydrogen, and sulphur, all but the highest fractions being colourless.

Some inconclusive experiments on the behaviour of various fractions of the oil towards mercuric chloride, bromine water, and iodine plus mercuric oxide are described. J. C. W.

Cevine and Sabadinine. Kurt Hess and Hermann Mohr (*Ber.*, 1919, **52**, [*B*], 1984—1988).—Investigation of the alkaloids themselves and of their hydrogen sulphates, potassium salts, aurichlorides, hydrochlorides, and monobenzoyl derivatives shows the

substances to be identical. The formula for the alkaloid is therefore $C_{27}H_{43}O_8N$. Certain corrections of the data recorded in the literature are given. The alkaloid crystallises with $3{\cdot}5H_2O$, and has m. p. 110°. The hydrogen sulphate $+2{\cdot}5H_2O$ has m. p. 250° (decomp.), after becoming discoloured at 210°. The potassium salt has the composition $C_{27}H_{41}O_8NK_2,EtOH$, or, more probably,

$$C_{27}H_{42}O_8NK,EtOK.$$

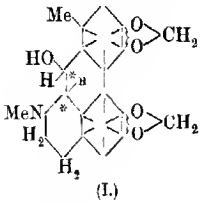
The hydrochloride forms anhydrous needles, m. p. 247°. The aurichloride from sabadinine has m. p. 162° (decomp.), whilst that from cevine has m. p. 167—168° (decomp.). The *monobenzoyl* derivative forms a white, amorphous powder, m. p. 195° (decomp.), after much previous softening. H. W.

Chelidoneum Alkaloids. J. Gadamer (*Arch. Pharm.*, 1919, 257, 298—303).—Oxidation of the three chelidoneum alkaloids, chelidonine and α- and β-homochelidonines, by means of mercuric acetate indicates that the former two are closely allied and that β-homochelidonine must be placed in the protopine group. Thus, both chelidonine and α-homochelidonine give up two atoms of hydrogen, passing into intensely yellowish-red salts of dehydro-bases which are of quaternary character, but exhibit such a marked tendency to the formation of colourless carbinol bases that they are converted into these even by the action of ammonia. From the fact that the optical activity is considerably increased, it must be assumed that the double linking which is introduced occupies a position adjacent to an asymmetric carbon atom. The optical activity of α-homochelidonine is of the same direction and order of magnitude as that of chelidonine, and the molecule contains, besides the two methoxyl groups, also a methylenedioxy-, a methylimino-, and an alcoholic hydroxyl group. On acylation it behaves similarly to chelidonine; by the action of acetic anhydride at a moderate temperature, acetylation occurs mainly at the oxygen atom (compare Tyrer, *Apoth.-Zeit.*, 1897, 442; Wintgen, A., 1901, i. 743), whilst at the boiling point it takes place almost exclusively at the nitrogen atom with elimination of water and ring-opening (compare Henschke, A., 1889, 62). On *O*-acetylation the optical activity is retained, whilst the *N*-acetyl compound is inactive.

When chelidonine methochloride or methosulphate is boiled with sodium hydroxide solution a strongly lævorotatory methine base and a small proportion of an apparently inactive methine base are formed.

On the basis of these observations, formula I is proposed for chelidonine and formula II for α-homochelidonine, each of these formulæ containing two asymmetric carbon atoms, marked with an asterisk. On oxidation to a didehydro-base, the asymmetry of the carbon atom contiguous to the nitrogen atom disappears, an optically active compound of formula III being obtained. The ring-opening on acetylation at the boiling point must yield first a compound of formula IV, this losing water to form compound V, which

still contains $1H_2O$ more than corresponds with an *N*-acetylanhydrochelidonine. Further loss of water is, however, less prob-



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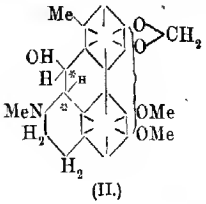

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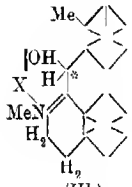

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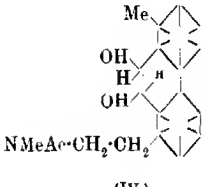

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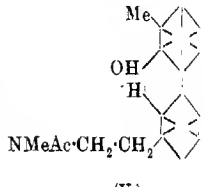
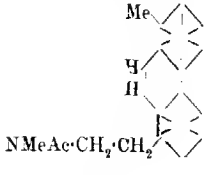


(V.)

able than auto-oxidation and auto-reduction, which should yield a compound of formula VI, but the analytical results do not correspond. The *N*-acetyl derivative is always accompanied by a small proportion of a colourless, quinone-like compound, which gradually turns inteusely red and is probably formed by oxidation. These conclusions are supported by the fact that the *O*-acetyl compound cannot be converted into the *N*-acetyl derivative by heating it, either alone or with acetic anhydride.

The lævorotatory methine base obtained by methylation of chelidoniue has probably the formula VII. On reduction, dide-hydrochelidonine is converted into chelidonine and, if the suggested formula is correct, two diastereoisomeric chelidonines should result, but their formation has not yet been verified. The free carbinol base must have the structure VIII. The position assumed for the methyl groups is not an entirely arbitrary one, since the alkaloids of the protopine group, which are to be referred to the same components (Bausteine), also contain at this place a side-chain of one carbon atom, this serving likewise to build up a heterocyclic ring.



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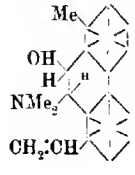

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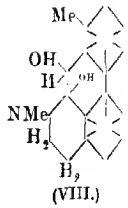

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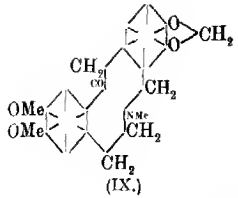
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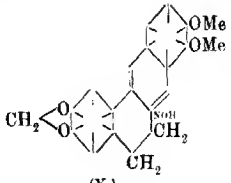
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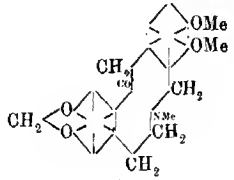
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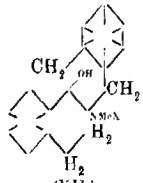
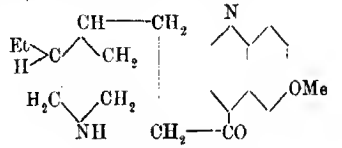

(XII.)

β-Homochelidonine, which resembles protopine and cryptopine in its physiological action, also behaves like these bases towards mercuric acetate; thus, two hydrogen atoms are replaced by an oxygen atom, so that one molecule of the base reduces four molecules of mercuric acetate to mercurous acetate. The product of the oxidation is relatively readily soluble in hot water, giving a slightly alkaline solution. This behaviour and the isomerism of cryptopine and β-homochelidonine indicate that the two alkaloids differ only as regards the relative positions of the methylenedioxy- and the two methoxy-groups. Assuming for cryptopine Perkin's formula (IX) (compare T., 1916, **109**, 831), which renders evident its close relationship to berberinium hydroxide (X), β-homochelidonine must be represented by formula XI. Confirmation of this formula is furnished (1) by the action of phosphoryl chloride, which yields *iso*-β-homochelidonine chloride, identical with dihydroberberine methochloride, and (2) by reduction to dihydro-β-homochelidonine and conversion of the latter, by means of phosphoryl chloride, into the chloride of the *iso*-compound, which exhibits complete identity with tetrahydroberberine methochloride.

These results supply a confirmation of Perkin's formulæ for protopine and cryptopine, but an objection to the formulæ for the three bases is the possession of a ten-membered ring, the formation of which in the vegetable organism is as yet unknown. This objection may be removed by the assumption for the salts, which alone are formed in plants, of formula XII. Formula XI or IX would then result only by anhydride formation from the carbinol base produced by the action of alkali. In agreement with this assumption is the fact that, with protopine, cryptopine, and, especially, β-homochelidonine, in presence of ammonium chloride, precipitation of the bases by ammonia takes place either not at all or only after some time.

Replacement of the name β-homochelidonine by *allo*cryptopine is recommended. T. H. P.

The Cinchona Alkaloids. XXI. Synthesis of Dihydroquinicine and β-4-Piperidylpropionic Acid. PAUL RABE and KARL KINDLER (*Ber.*, 1919, **52**, [*B*], 1842—1850. Compare A., 1919, i, 34).—I. *Synthesis of Dihydroquinicine* (*Dihydroquinotoxine*).—Ethyl quinate and ethyl *N*-benzoylhomocincholeuponate (*ibid.*) are condensed by means of sodium ethoxide in benzene to form a β-ketonic ester, which is deprived of the benzoyl and carbethoxyl groups by boiling with 17% hydrochloric acid, thus giving dihydroquinicine,



II. *Synthesis of β-4-Piperidylpropionic Acid.*—4-Methylpyridine is heated with chloral and zinc chloride at 85—90° for several hours, and thus converted into "*γ-chloralpicoline*" [γγγ-*trichloro-α-4-pyridylpropan-β-ol*], $CCl_3{\cdot}CH(OH){\cdot}CH_2{\cdot}C_5H_4N$, glistening crystals, m. p. 166° (corr.); *platinichloride*, orange needles, m. p. 250° (corr., decomp.), *aurichloride*, yellow crystals, m. p. 189° (corr., decomp.). This compound is mixed with ice-cold alcoholic potassium hydroxide, and the temperature then allowed to rise, when hydrolysis proceeds vigorously, the product being *β-4-pyridylacrylic acid*, $C_5H_4N{\cdot}CH{:}CH{\cdot}CO_2H$, pale reddish-brown crystals, m. p. 296° (corr., decomp.); *hydrochloride*, $1H_2O$, large, brown crystals, m. p. 243—244° (corr.), *aurichloride*, yellow needles, m. p. 235° (corr., decomp.). The acid is reduced by sodium in boiling amyl alcohol to *β-4-piperidylpropionic acid*,

$$C_5H_{10}N{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H;$$

the acid was not isolated, but converted into the *ethyl* ester, b. p. 145°/15 mm., *platinichloride*, orange crystals, m. p. 190° (corr., decomp.). J. C. W.

Preparation of Nitriles from Quinotoxines. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 313321; from *Chem. Zentr.*, 1919, iv, 499).—Oximinoacidyl derivatives of dihydroquinotoxine are treated with acidylating agents in the presence of alkali. Reaction occurs in accordance with the scheme:

$$R{\cdot}C_9H_5N{\cdot}CO{\cdot}C(N{\cdot}OH){\cdot}CH_2{\cdot}CH\langle\begin{matrix}CH_2\text{---}CH_2\\ CHR'{\cdot}CH_2\end{matrix}\rangle N{\cdot}Acyl \longrightarrow$$

$$R{\cdot}C_9H_5N{\cdot}CO_2H + CN{\cdot}CH_2{\cdot}CH\langle\begin{matrix}CH_2\text{---}CH_2\\ CHR'{\cdot}CH_2\end{matrix}\rangle N{\cdot}Acyl$$

(R = H or OMe; R' = Et or Me.)

Cinchotoxine is converted by benzoyl chloride in the presence of

alkali into a *benzoyl* derivative, m. p. 124°, which, when treated with amyl nitrite and sodium alkyloxide, yields a crystalline *oximino*-derivative, m. p. 175—177°; the yellowish-red solution of the latter in sodium hydroxide solution (5%) is transformed by toluene-*p*-sulphonyl chloride at 45° into *benzoylcincholeupono-nitrile*, colourless crystals, m. p. 62°. *Acetylcinchotoxine* is formed as a pale yellow, viscous mass by the treatment of cinchotoxin (quinicine) with acetyl chloride, and, without being further purified, is converted into *oximinoacetylcinchotoxine*, from which *acetylmeroquinenonitrile*, almost colourless, viscous oil, is prepared by the action of benzoyl chloride and sodium hydroxide solution (5%). The nitriles are intended as initial materials for pharmaceutical preparations. H. W.

The Oxidation of Morphine. Constantin Kollo (*Bul. Soc. chim. România*, 1919, 1, 3—9).—Solutions of morphine hydrochloride when sterilised in an autoclave at 120° undergo some decomposition, as shown by the brown colour produced in the liquid. The change occurring is the formation of oxydimorphine (*ψ*-morphine) and morphine oxide in the proportion of 9 : 1, together with traces of a base said to be methylamine. The percentage of morphine decomposed increases with the temperature to which the solution is heated.

It is suggested that morphine hydrochloride undergoes partial dissociation, and that in the free morphine the group :NMe reacts with the water, giving methylamine and hydrogen peroxide, the latter then acting as an oxidising agent. W. G.

Morphine Alkaloids. VI. The Relative Stability of the Nitrogen Ring in Morphine. Julius von Braun (*Ber.*, 1919, 52, [*B*], 1999—2011).—It has recently been shown (A., 1918, i, 184, 268) that the gradations of stability exhibited by six of the seven classes of bases which have been examined from the point of view of the rupturing of the cyclic system are the same whether the action be effected by Hofmann's method or by cyanogen bromide. Dihydroindole appears to be an exception, since it proves to be one of the most stable systems in the Hofmann degradation, but one of the weakest towards cyanogen bromide. The present communication contains an account of the behaviour of a number of substances containing the grouping, aromatic nucleus, C·C·N, which is present in the morphine molecule. This appears to be extraordinarily resistant to cyanogen bromide, but to be attacked with remarkable ease by bases.

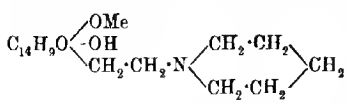
The nomenclature of some of the substances which have been obtained offers certain difficulties, to overcome which the author proposes to designate the group, $C_{11}H_9O(OMe)(OH)\cdot CH_2\cdot CH_2-$, methylmorphimethyl.

Norcodeinium piperidinium iodide, m. p. 272°, is prepared by the action of norcodeine on αε-di-iodopentane in alcohol, or, preferably, in chloroform (the *platinichloride* is a crystalline powder,

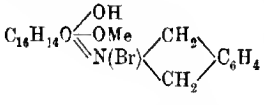
m. p. 215°; the corresponding *dihydronorcodeinium piperidinium iodide* has m. p. 271°), and is converted by cold aqueous sodium hydroxide solution into *methylmorphimethylpiperidine* (annexed formula), stout rods, m. p. 93—94° (the hygroscopic *hydrochloride*, the *platinichloride*, m. p. 174°, the oily *methiodide*, and the *acetyl* derivative, m. p. 87°, are described). It cannot readily be shown that the disruption of the nitrogen atom has occurred from the morphine and not from the piperidine half of the molecule by the use of acetic anhydride, but the required evidence is readily furnished by the application of cyanogen bromide to the acetyl derivative, which yields *ε-bromoamylcyanoacetylmethylmorphimethylamide*,

$$C_{14}H_9O(OMe)(OAc)\cdot CH_2\cdot CH_2\cdot N(CN)[CH_2]_5Br,$$

colourless leaflets, m. p. 133—134°.



Norcodeine and *o*-xylylene bromide similarly yield *norcodeinium-dihydroisoindolium bromide* (annexed formula), long needles, m. p. 262° (*platinichloride*, m. p. 233°), which is transformed by alkali into *methylmorphimethyldihydroisoindole*, m. p. 110°, the salts of which show little tendency to crystallise. The crystalline *acetyl* derivative, shining leaflets, m. p. 146°, yields, however, a *hydrochloride*, colourless leaflets, m. p. 224°, and a *methiodide*, colourless leaflets, m. p. 163°. The course of fission is already established by the nature of the product, and is confirmed by the action of cyanogen bromide on the acetyl derivative, which yields *ω-bromoxylylcyanoacetylmethylmorphimethylamine*, colourless crystals, m. p. 153°.



The interaction of norcodeine and *ββ'*-di-iodoethyl ether leads to the formation of *norcodeinium-morpholinium iodide*, long needles, m. p. 255—256° (*platinichloride*, m. p. 216°), which is converted by alkali into *methylmorphimethylmorpholine*; since the latter is oily and does not yield well-crystallised salts, it was identified as the *acetyl* derivative, m. p. 118—120° (*platinichloride*, m. p. 177°). Cyanogen bromide transforms the acetyl compound into an oily product, which doubtless consists mainly of the expected bromo-compound, but could not be isolated in the pure state.

H. W.

Ormosine and Ormosinine, Two New Alkaloids from Ormosia dasycarpa. Kurt Hess and Fritz Merck (*Ber.*, 1919, **52**, [*B*], 1976—1983).—Ormosine has been previously isolated by Merck from *Ormosia dasycarpa*, Jacks, a leguminous plant growing in Venezuela. Its physiological relationship to the morphine alkaloids has been demonstrated by Harnack, but the authors find that it is not allied chemically to these substances, and, indeed,

occupies a unique position among alkaloids. In addition, they have isolated ormosinine from the same source, the yield of the former amounting to 0·15% and of the latter to 0·023% of the dried seeds; these substances, however, only represent a fraction of the total alkaloidal content.

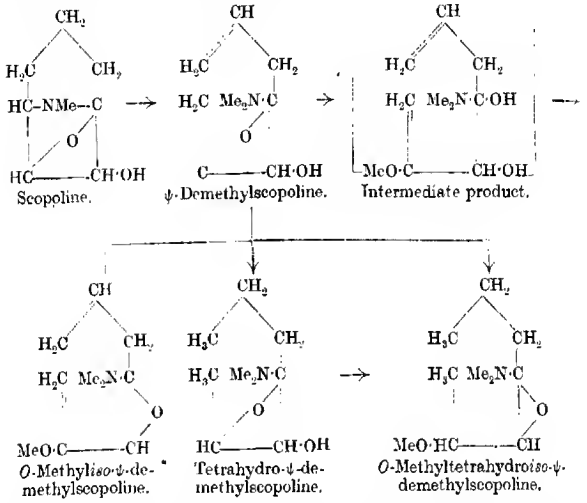
Isolation of the alkaloids is effected by extracting the crushed seeds with alcohol, evaporation of the solvent in a vacuum, and extraction of the residue with water; the aqueous extract is made alkaline with ammonia and extracted with ether. The ethereal solution is shaken with powdered sodium carbonate, after which the solvent is removed, leaving a crystalline residue, from which ormosinine is isolated by taking advantage of its sparing solubility in alcohol, whilst ormosine separates from the alcoholic solution on addition of water.

Ormosine, $C_{20}H_{33}N_3$, crystallises with 3—4H_2O in long needles, m. p. 85—87°, and is readily soluble in alcohol or chloroform. When preserved over sulphuric acid, it loses its water of crystallisation and forms a colourless, gummy mass, which again becomes crystalline when brought into contact with water. It is sensitive towards rise in temperature, and, at 100°, is converted into a viscous oil, which does not recombine with water. With methyl iodide, it gives an abnormally constituted *methiodide*, $C_{24}H_{45}N_3I_2$, long needles, m. p. 245—250° (slow decomp.). The *picrate* has m. p. 178° (decomp.). The *hydrochloride*, *hydrobromide*, and *aurichloride* are amorphous. The *aurichloride* of the *methochloride*, $C_{24}H_{47}N_3Cl_2,2AuCl_3$, forms yellow crystals, which change at 90°.

Ormosinine, $C_{20}H_{33}N_3$, crystallises in well-defined, anhydrous cubes and short prisms, m. p. 203—205°. It yields a normally constituted *methiodide*, $C_{21}H_{36}N_3I$, colourless needles, m. p. 245° (slow decomp.), and a *picrate*, $C_{32}H_{39}O_{14}N_9,4H_2O$. H. W.

Scopoline. IV. Fission of Scopoline by Hofmann's Method of Degradation and Elucidation of the Constitution of Scopoline. Kurt Hess (*Ber.*, 1919, **52**, [*B*], 1947—1975).—Previous investigations (A., 1918, i. 404, and previous abstracts) have largely elucidated the constitution of scopoline, leaving in doubt, however, the mode of attachment within the molecule of one valency of one of the oxygen atoms. In the hope of deciding this point, the author has applied Hofmann's method to scopoline. Reaction, however, occurs abnormally, since the product, ψ-demethylscopoline, contains two double bonds, as is evidenced by its ready conversion into a tetrahydro-derivative. Moreover, the process throws no light on the point in question, since the oxygen linking appears to remain intact. When, however, ψ-demethylscopoline is further subjected to the Hofmann degradation, it gives *O*-methyl*iso*-ψ-demethylscopoline, the ammonium base yielding the tertiary amine and methyl alcohol, which adds itself at the ethylene oxide group. Elimination of water occurs from the methylated polyhydroxy-alcohol in such a manner as to form a new ethylene oxide group.

This view is strengthened by the formation of a similarly constituted compound from tetrahydro-ψ-demethylscopoline, which is also produced by the reduction of *O*-methyl*iso*-ψ-demethylscopoline itself. The most ready explanation of these reactions lies in the hypothesis that the ethereal oxygen atom is directly united to that carbon atom to which the nitrogen group is attached, since, if it were attached to one of the other possible carbon atoms, it is difficult to see why the oxygen bridge should be disturbed by a process which only affects the amino-group. The reactions are consequently shown by the schemes:



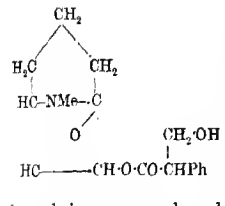
Corresponding with the two asymmetric carbon atoms of ψ-demethylscopoline, the latter is found to exist in two diastereoisomeric racemic forms (α- and β-), both of which have been isolated and used in the series of degradations. During hydrogenation, a third asymmetric carbon atom is developed, so that yet another isomeride is formed.

Scopoline methiodide is converted into the corresponding hydroxide, which is distilled under diminished pressure, whereby an oil, b. p. 118—121°/9 mm., is obtained in good yield, which consists of a mixture of approximately equal amounts of α- and β-*ψ-demethylscopoline*. The α-form crystallises in needles or prisms, m. p. 67—69° (*picrate*, prismatic needles, m. p. 152—153°; *methiodide*, m. p. 248° [decomp.]; *benzoyl* derivative, indistinct crystalline needles, m. p. 120°, the *hydrochloride* of which [+3EtOH] has m. p. 214° [decomp.], after much previous softening). The β-form has b. p. 135—140°/15—16 mm. (*picrate*, large, cubic crystals, m. p. 205° [decomp.]; the *methiodide* is oily).

Reduction of *aψ*-demethylscopoline by hydrogen in the presence of colloidal platinum yields a product, b. p. 143—145°/30 mm., which solidifies completely to a mass of long needles, but which is found to be a mixture of two stereoisomerides, since it gives two *picrates*, m. p.'s 182° and 128° respectively, and two *methiodides*, m. p. 209° and oily. The corresponding *β*-base also appears to yield two stereoisomeric *tetrahydro-βψ-demethylscopolines* (b. p. of mixture 135°/27 mm.), the *methiodides* of which are oily. *O-Methyltetrahydroiso-aψ-demethylscopoline* is obtained by Hofmann's method from the tetrahydro-*α*-base, and forms an oil, b. p. 122—125°/17 mm., which partly crystallises when preserved, and probably consists of a mixture of isomerides; the *picrate* has m. p. 163°. The corresponding *β*-derivative has b. p. 126—130°/23 mm. (*picrate*, m. p. 183—184°; *platinichloride*, hexagonal crystals, m. p. 200° [decomp.]).

The degradation of *α*- and *β*-*ψ*-demethylscopoline does not occur very smoothly, and in addition to *O-methyliso-aψ-demethylscopoline*, pale yellow oil, b. p. 123°/14 mm., and *O-methyliso-βψ-demethylscopoline*, viscous, yellow oil, b. p. 140°/28 mm., a highly refractive volatile *oil*, $C_7H_8O_2$, of characteristic odour, b. p. 88—92°/11 mm., is obtained. A *picrate*, needles, m. p. 142—143°, was isolated from the product of the degradation of the mixed bases.

The oxygen bridge in *aψ*-demethylscopoline, unlike that in scopoline itself (A., 1916, i. 286), does not appear to be opened by treatment with hydrogen bromide in glacial acetic acid solution, the products of the action being the *hydrobromide* of the original base, prisms, m. p. 250° (decomp.), and resinous matter.



Attempts further to degrade the tetrahydro-*O*-methyliso-*ψ*-demethylscopolines were unsuccessful, the bases being recovered unchanged.

As a consequence of the work on scopoline, the annexed formula may now be ascribed to scopolamine. H. W.

Strychnos Alkaloids. XXV. Rearrangement of Strychninolone into Isomeric Forms. Hermann Leuchs and Walter Bendixsohn (*Ber.*, 1919, **52**, [*B*], 1443—1453. Compare A., 1914, i, 861).—When the *a*-form of strychninolone, $C_{19}H_{18}O_3N_2$, is shaken with 0·5*N*-sodium hydroxide for a few days, about 80% of it is changed into strychninolone-*b*, massive crystals, m. p. 228°, $[\alpha]_D^{20}$ −37·3°. The alkali contains about 6% of the by-product, $C_{38}H_{36}O_4N_2$, m. p. 235—270°, $[\alpha]_D^{20}$ +21·5°, which was also formed during the fission of strychninolic acid. A similar transformation is effected by heating the *a*-form with methyl-alcoholic ammonia in a sealed tube. The products are the *b*-form, a new isomeride which is less soluble in methyl alcohol, namely, *strychninolone-c*, hexagonal prisms or pointed and twinned leaflets, m. p. 251—252°,

$[\alpha]_D^{13}$ −176·1°, and two isomeric amines. These are *aminodihydrostrychninolone*-I, $C_{19}H_{21}O_3N_3,H_2O$, polyhedric tablets or columns, m. p. 185—191° (decomp.), which forms a sparingly soluble *nitrate*, m. p. 261—263° (decomp.), $[\alpha]_D^{15}$ −51·6°, and a *phenylcarbamide*, $C_{26}H_{26}O_4N_4$, m. p. 240—241°, and again at 295—300°, and also *aminodihydrostrychninolone*-II, stout needles, m. p. 236—239° (decomp.), $[\alpha]_D^{15}$ −66·6°, which forms a soluble nitrate.

When strychninolone-*b* is covered with 12*N*-hydrochloric acid, it changes into the salt of an *amino-acid*, $C_{19}H_{20}O_4N_2,4H_2O$, broad needles, m. p. 239—240° (decomp.), which is identical with the strychninolone-hydrate-II, already described (A., 1910, i, 768). Strychninolone-*b* also forms an *acetate*, $C_{21}H_{20}O_4N_2$, when heated with acetic anhydride and sodium acetate. This crystallises in prisms with 1MeOH, m. p. 140° (decomp.), and then 214°, $[\alpha]_D^{20}$ −37·6°, and may be formed by heating acetylstrychninolone-*a* with acetic anhydride. J. C. W.

Strychnos Alkaloids. XXVI. Degradation of Bromostrychnine and Dihydrostrychninonic Acid, and the Bromination of the Fission Products of Strychnine. Hermann Leuchs and Dorothea Ritter (*Ber.*, 1919, **52**, [*B*], 1583—1593). —Bromostrychnine (Beckurts, A., 1885, 911) is most conveniently made by adding bromine water to strychnine dissolved in hydrobromic acid, for it separates as the hydrobromide (solubility at 15°, 1%), leaving the salt of the unchanged base in solution. When oxidised by permanganate at −10° to 15° in acetone solution, it yields bromostrychninonic acid (soluble in chloroform; A., 1910, i, 766) and insoluble *bromodihydrostrychninonic acid*,

$$C_{21}H_{21}O_6N_2Br.$$

This crystallises in minute, hexagonal leaflets, m. p. 310° (decomp.), $[\alpha]_D^{20}$ −19·7° (in 0·1*N*-sodium hydroxide), may also be obtained by brominating dihydrostrychninonic acid, and is gradually hydrolysed by *N*-alkali hydroxide in the cold to glycollic acid and a *compound*, $C_{19}H_{17}O_3N_2Br$, which crystallises from alcohol in slender needles, m. p. 273°, $[\alpha]_D^{20}$ −24·2°.

Dihydrostrychninonic acid, obtained in 6% yield by oxidising strychnine with permanganate in boiling acetone, is hydrolysed by *N*-alkali hydroxide to two isomerides, according to the conditions. In the cold, the product is iso*strychninolone*-I, $C_{19}H_{18}O_3N_2$, colourless pyramids, m. p. 246—247°, $[\alpha]_D^{20}$ +46·4°, which yields the above compound, $C_{19}H_{17}O_3N_2Br$, on bromination. At 100°, the product is iso*strychninolone*-II, long, woolly needles, not molten at 310°, $[\alpha]_D^{20}$ −126°, giving a cornflower-blue colour with chromic and sulphuric acids, and a very sparingly soluble *bromo*-derivative, m. p. 280°.

Strychninonic acid yields the same acid on bromination as bromostrychnine gives on oxidation, namely, bromostrychninonic acid. The *methyl* ester of this, $C_{22}H_{21}O_6N_2Br$, has m. p. 230—231°, and the *ethyl* ester, m. p. 247° (corr.). The acid is reduced by sodium amalgam to *bromostrychninolic acid*, $C_{21}H_{21}O_6N_2Br$, minute prisms.

decomp. 265—270°, which is gradually hydrolysed by *N*-sodium hydroxide to glycollic acid and bromostrychninolone-*a* (below).

The *a*- and *b*-forms of strychninolone yield on bromination *bromostrychninolone*-a, $C_{19}H_{17}O_3N_2Br$, stout tablets, m. p. 254—256°, $[\alpha]_D^{20}$ −62·2°, and *bromostrychninolone*-b, stout prisms or tablets, m. p. 233—235°, $[\alpha]_D^{20}$ −72·8°. J. C. W.

Synthesis of 2-*n*-Butylpyrrolidine. Remarks on the Work of E. Blaise and Houillon on the Transformation of the Higher Alkylenediamines into Cyclic Mono-imines. Kurt Hess (*Ber.*, 1919, **52**, [*B*], 1636—1641).—2-Pyrryl propyl ketone (Oddo, A., 1910, i, 426) is reduced by sodium and alcohol to α-2-pyrrolidylbutyl alcohol (A., 1916, i, 68), the constitution of which has been proved (A., 1917, i, 351, 352), and this is heated with hydriodic acid (D 2·0) and red phosphorus at 125—135°. 2-n-*Butylpyrrolidine* is a colourless oil, b. p. 154—156°/753 mm., which has a very similar odour to coniine, and is only sparingly soluble in water. The *platinichloride* forms stout prisms, m. p. 178°, and the *aurichloride* is an unstable, egg-yellow, flocculent powder, m. p. 145°. When heated with formaldehyde and formic acid, the base yields 1-*methyl*-2-n-*butylpyrrolidine*, b. p. 154—155°/15 mm., which forms a *platinichloride*, long, prismatic tablets, m. p. 215°, and an *aurichloride*, m. p. 190°.

The base described by Blaise and Houillon as 2-*n*-butylpyrrolidine (A., 1906, i, 692) must have had some other constitution.

J. C. W.

Pyrrolidine Derivatives. V. Preparation of the Three Hydroxyprolines which are Stereoisomerides of the Natural Hydroxyproline. Hermann Leuchs and Karl Bormann (*Ber.*, 1919, **52**, [*B*], 2086—2097).—The work is a continuation of that described previously (Leuchs and Brewster, A., 1913, i, 449).

dl-Hydroxyproline (*a*) is resolved by crystallisation of the quinine salt of its phenylcarbamide, as described previously; the specific rotation of the synthetic *l*-hydroxyproline (*a*) in aqueous solution cannot be raised above −75·7°, a value which agrees well with that recorded previously, but is lower than the sole datum (−81°) for the natural acid. d-γ-*Hydroxyprolinephenylcarbamide* (*a*) has m. p. 175°, $[\alpha]_D^{27}$ +37° (in water as ammonium salt); d-*hydroxyproline* (*a*) has m. p. about 274°, $[\alpha]_D^{21}$ +75·2° in aqueous solution. The corresponding *hydantoin* has m. p. 130—131° (anhydrous), ca. 70° (+$2H_2O$), $[\alpha]_5^{25}$ +49·9°, for the anhydrous substance in water.

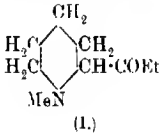
dl-γ-Hydroxyprolinephenylcarbamide (*b*) is similarly resolved by means of quinine, as previously described; *l*- and *d*-hydroxyproline (*b*) have now been obtained in the crystalline form, slender needles, m. p. 238—241° (decomp.), $[\alpha]_5^{15}$ −58·1° and +58·6° respectively.

The product obtained by racemising the natural hydroxyproline with barium hydroxide appears to be identical with that obtained

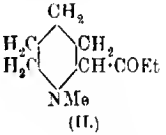
by mixing equal weights of *l*-hydroxyproline (*a*) and *d*-hydroxyproline (*b*); it appears that a change of configuration only occurs at the *a*-carbon atom, whilst the γ-carbon atom remains unaffected.

Derivatives of *dl*-hydroxyproline (*a*) and (*b*) with phenylthiocarbimide are described, but are unsuitable for purposes of resolution owing to the ease with which they pass into anhydrides which are either thiohydantoins or thioazlactones; *γ-hydroxyprolinephenylthiocarbamide* forms nodular crystals, and when crystallised from warm water or heated at 63° readily gives the corresponding *anhydride*, slender needles, m. p. 145—148°; its m. p. is the same as that of the anhydride; *γ-hydroxyprolinephenylthiocarbimide* (*b*), m. p. 155—156°, is rather more stable than the *a*-derivative. The corresponding *anhydride* crystallises in small needles, m. p. 146—148°. H. W.

The Asymmetric, Tervalent Nitrogen Atom. II. New Transformations of *dl*-Methylconhydrinone and the Conversion of *d*-Conhydrinone into *dl*-α-2-Pyrrolidylbutan-β-one. KURT HESS (*Ber.*, 1919, **52**, [*B*], 1622—1636. Compare A., 1919, i, 345).—In the former paper, it was shown that α-1-methyl-2-piperidylpropan-α-one exists in two stereoisomeric forms, methyl-*iso*pelletierine (I) and methylconhydrinone (II).



(I.)



(II.)

A further proof of the close relationship between these bases is now given, namely, the fact that when their hydrazones are boiled with sodium ethoxide solution they both yield *dl*-methylconiine.

In the further elucidation of this unusual case of isomerism, it is found that during changes at the asymmetric nitrogen atom, the particular configuration is preserved, but that changes at the propyl residue, that is, at the asymmetric carbon atom, lead to the same products in both cases.

As a reaction of the former type may be mentioned the dimethylation by means of ethyl azodicarboxylate. This leads to the production of *iso*pelletierine on the one hand and dl-*conhydrinone*, b. p. 93—94°/10 mm., on the other. Furthermore, the ethylurethane of *d*-conhydrinone (*loc. cit.*) is isomeric with the *ethylurethane* of *iso*pelletierine, this having now been obtained as a viscous oil, b. p. 165—170°/13 mm., by the action of ethyl chloroformate on the base in ether, under the influence of powdered potassium carbonate.

A most remarkable difference between these isomeric ethylurethanes is described. When boiled with aqueous-alcoholic sodium hydroxide, the *iso*pelletierine derivative is slowly hydrolysed to *iso*pelletierine and resinous products, whereas the *d*-conhydrinone

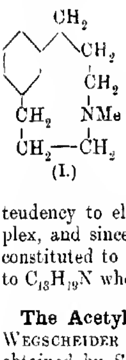
derivative is quickly and almost quantitatively converted into dl-α-2-*pyrrolidylbutan-β-one* (annexed formula). This oil has b. p. 95—97°/10 mm., responds readily to the pine-shaving test, forms a *picrate*, bundles of needles, m. p. 155°, is converted by heating with formaldehyde and formic acid into *α-l-methyl-2-pyrrolidylbutan-β-one*, b. p. 112—115°/22 mm. (*hydrochloride*, m. p. 153°; *platinichloride*, m. p. 205°; *methiodide*, long spikes, m. p. 213—215°), and yields a *hydrazone*, b. p. 135—140°/15 mm., which is reduced by heating with sodium ethoxide solution at 150—170° to 2-butylpyrrolidine (see this vol., p. 85). J. C. W.

Additive Compounds of Acyl Chlorides and Tertiary Amines. Karl Freudenberg and Daniel Peters (*Ber.*, 1919, **52**. [*B*], 1463—1468).—In many cases, chloroform is an excellent medium in which to study reactions between acyl chlorides and tertiary amines, for the additive compounds readily separate, leaving such by-products as the amine hydrochlorides and dehydracetic acid in solution, and, furthermore, there is much less danger of the precipitate absorbing atmospheric moisture during filtration than when ether is used as the diluent (compare Dehn. A., 1912, i, 833; 1914, i, 1169). The true additive compounds are extremely sensitive to water and alcohol, especially in those cases in which intermolecular expulsion of hydrogen chloride is possible, and this is why so few genuine compounds of this type have been described.

Oxalyl chloride and pyridine form a compound in the ratio 1:2 (Jones and Tasker, P., 1908, **24**, 271), which separates in yellow, sandy crystals and evolves carbon monoxide and dioxide on exposure to moist air. Acetyl chloride and pyridine unite in the ratio 1:1 (Dennstedt and Zimmerman, A., 1886, 368), the compound dissolves in the chloroform if moisture is allowed to enter, and reacts with alcohol to form pyridine hydrochloride and ethyl acetate. The compound given by hexamethylenetetramine and benzoyl chloride is also decomposed by alcohol, which Hartung overlooked when he spoke of it as being somewhat soluble in this medium (A., 1892, 1173). J. C. W.

Ring Closure in the Meta-position in the Benzene Series. I. Reduction of Julolidine Methochloride. Julius von Braun and Ludwig Neumann (*Ber.*, 1919, **52**. [*B*]. 2015—2019).—It has been shown previously (von Braun, Heider, and Wyczatkowska, A., 1919, i, 40) that the reduction of julolidine methochloride by sodium amalgam leads to the formation of a base, $C_{13}H_{19}N$. The latter has now been isolated as a colourless oil, b. p. 87—89°/0·01 mm., which can be preserved unchanged in a closed vessel (the methiodide has m. p. 178° instead of 200°, as previously recorded). When this is converted into its methiodide, treated with silver oxide, and the product is distilled under greatly

diminished pressure, two fractions are obtained: (1) unchanged base mixed with a certain amount of an unsaturated base, and (2) an oxy-*base*, $C_{14}H_{23}ON$, syrupy liquid, b. p. 145—147°/0·01 mm. The *hydrochloride*, *platinichloride*, *picrate*, and *methiodide* of the latter are oily, but the *platinum* salt of the methochloride forms orange needles, m. p. 165°. The nitrogen atom of the base, like that of the original amine, is not attached to the aromatic nucleus, neither is oxygen present as phenolic hydroxyl. In confirmation of these facts, it is found that only *iso*phthalic acid is formed when it is oxidised. It follows, therefore, that the base $C_{13}H_{19}N$ must contain the complex $C_6H_{12}NMe$ in the form of a closed chain united to two carbon atoms of the benzene nucleus which are in the meta-position to one another. The structure of the complex can be deduced with considerable probability from the following facts: (1) the nitrogen is probably in the γ-position to the benzene nucleus, since attempts to apply Hofmann's process to the degradation of the oxy-base were unsuccessful, and (2) the production of a tertiary hydroxy-amine instead of an unsaturated amine in Hofmann's reaction is only probable if a primary alcoholic group can be developed. The grouping $-CH_2\cdot CH_2\cdot CH_2\cdot NMe\cdot CH_2-$ is therefore probably present in the amine, $C_{13}H_{19}N$, and the annexed formulæ are thus possible. The second of these is, however, very improbable, since the corresponding hydroxy-base would show a great tendency to eliminate water and form a methylated styrene complex, and since, also, α-methyl-lilolidine, which is very analogously constituted to julolidine, does not yield a trace of a base analogous to $C_{13}H_{19}N$ when its methochloride is reduced.



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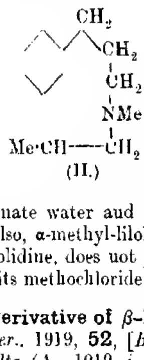


(II.)

H. W.

The Acetyl Derivative of β-Indoxylcinnamic Acid. RUD. WEGSCHEIDER (*Ber.*, 1919, **52**, [*B*], 1705).—The acetyl derivative obtained by Scholtz (A., 1919, i, 96) may be represented by the formula $C_6H_4\cdot C(OAc)$——O / NH—CH·CPh:CH·CO. J. C. W.

Modification of Skraup's Synthesis for Preparing Quinoline Bases: their Conversion into Stannichlorides. J. G. F. DRUCE (*Chem. News*, 1919, **119**, 271—273).—The method adopted for the synthesis of quinoline from aniline stannichloride (A., 1918, i, 535) has been applied successfully, although with diminished yields, to the synthesis of homologues of quinoline. Thus *o*-, *m*-, and *p*-toluidine stannichlorides treated with glycerol and sulphuric acid heated at 120° for two to three hours and then diluted and diazotised gave, respectively, 8-, 7-, and 6-methylquinoline in yields varying from 25% with the meta- to 70% with the para-compound

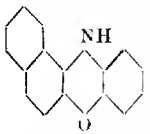
On the other hand, *m*- and *p*-phenylenediamine stannichlorides gave extremely poor yields of the phenanthrolines. The stannichlorides of the methylquinolines were prepared by dissolving crystalline stannic chloride in hydrochloric acid solutions of the bases, and they crystallised out on cooling. *6-Methylquinoline stannichloride* forms white plates, m. p. 248°, *7-methylquinoline stannichloride*, pale yellow needles, m. p. 229°, and *8-methylquinoline stannichloride*, white needles, m. p. 252° (with decomp.). *m-Toluidine stannichloride*, prepared in an analogous fashion, formed pearly-white plates, soluble in cold water and alcohol, m. p. 76°. *m*-Toluidine stannichloride crystallised in pale pink, nacreous plates, m p. 284°. A rapid method for the estimation of chlorine in these and other tin salts of aliphatic and aromatic bases was devised, consisting in simple titration with *N*/10-sodium hydroxide, using phenolphthalein as indicator. Good results were obtained with aromatic compounds, but the stronger alkalinity of the aliphatic bases interferes with the end-point to some extent, and less accurate results are consequently obtained. G. F. M.

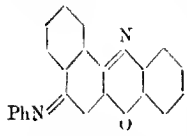
Preparation of Indigoid Dyes. Adolf Jolles (D.R.-P. 305558; from *Chem. Zentr.*, 1919, iv, 619).—Aromatic hydroxy-derivatives containing a phenolic hydroxyl group are oxidised in the presence of indoxyl or indoxylic acid. Thus a mixture of "*2-naphthalene-2-indolindigo*" and "*4-naphthalene-2-indole-indolignone*" (separable by extracting the latter with boiling dilute sodium hydroxide solution) is obtained when indoxyl and α-naphthol dissolved in acetic acid are oxidised by a solution of ferric chloride in hydrochloric acid. A solution of the 20% indoxylic acid fusion and α-anthrol, when similarly treated, yields "2-anthracene-2-indolindigo" (identical with the dye prepared from isatin-α-anilide and α-anthrol). H. W.

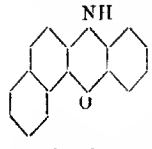
Synthesis of 2 : 3-Pyridinoacenaphthene. Alois Zinke and Emmy Raith (*Monatsh.*, 1919, **40**, 271—276).—The experiments were undertaken with the object of ultimately preparing an α-naphthaquinoline-6 : 7-dicarboxylic acid; the anhydride of such an acid is described, but the yields are not sufficiently satisfactory to permit further work.

2 : 3-Pyridinoacenaphthene (annexed formula), colourless, ice-like crystals, m. p. 67° (uncorr.), is obtained by the action of concentrated sulphuric acid, glycerol, and nitrobenzene on 3-aminoacenaphthene. The *hydrochloride*, long, pale yellow needles, m. p. 305°, the *sulphate*, small, yellow needles, m. p. 238°, and the *methiodide*, yellow needles united in clusters, which does not melt below 315°, are described. Oxidation of the base or of its salts by chromic acid in acetic acid solution leads to the formation of α-naphthaquinoline-6 : 7-dicarboxylic anhydride, long, red needles, m. p. 317°. H. W.

1 : 2-Naphthaphenazoxines. HENRI GOLDSTEIN and ZDENKA LUDWIG-SEMELITCH (*Helv. Chim. Acta*, 1919, **2**, 655—662. Compare Kehrmann and Neil, A., 1915, i, 303).—1 : 2-*α-Naphthaphenazoxine* (annexed formula), yellow solid, m. p. 107° (decomp.), is prepared by gradually heating a mixture of *α*-amino-*β*-naphthol hydrochloride and *o*-aminophenol to 260° in a current of carbon dioxide; it is a very unstable substance which cannot be purified by crystallisation, the physical properties recorded being those of a small amount of material which had sublimed during the preparation. The *acetyl* and *benzoyl* derivatives could not be obtained in the crystalline state. The compositiou of the substance is deduced from the conversion of the crude product into naphthaphenazoxone, on the one hand, and into 6-*phenylnaphthaphenoxazime* (annexed formula) on the other. The constitution of the latter substance is established by its synthesis from *o*-aminophenol hydrochloride and anilino-*β*-naphthaquinone; it forms orange needles, m. p. 215°, and behaves as a very weak base. The *hydrochloride*, slender, red needles with green reflex, and the *platinichloride*, small, brown crystals, are described.

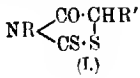




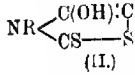


1 : 2-*β-Naphthaphenazorine* (annexed formula) is formed, together with the *α*-isomeride, by heating a mixture of *αβ*-dihydroxynaphthalene and *o*-aminophenol. It forms yellow crystals, which darken in the air at about 110° and melt in a closed tube at 127—128°. The *acetyl* derivative could not be caused to crystallise. It is converted by aniline hydrochloride and ferric chloride into 3-*phenylisonaphthaphenoxazime*, which is a weak, unstable base; the *hydrochloride* and *platinichloride* are described. H. W.

Stereochemistry of Rhodanines. II. STEN KALLENBERG (*Ber.*, 1919, **52**, [*B*], 2057—2071. Compare A., 1917, i, 279). It is found that rhodanines with a tertiary *β*-carbon system and such as contain the asymmetric carbon atom outside the thiazole ring exhibit normal properties, and can be obtained in stable active forms. Rhodanines in which a hydrogen atom is united to the asymmetric *β*-carbon atom cannot be isolated in the active state. The most obvious explanation is to regard them as thiazolines (II) instead of thiazolidines (I), although it is also possible that a keto-enolic equilibrium is set up.



(I.)



(II.)

The condensation of *d*-thiolactic acid and phenylthiocarbimide

leads to the formation of *r*-3-phenyl-5-methylrhodanine, m. p. 114—116°.

5-*Methyl*-3-*ethylrhodanine*-5-*acetic acid*,

$$NEt\langle \begin{matrix} CO\cdot CMe\cdot CH_2\cdot CO_2H \\ | \\ S-S \end{matrix}$$

is prepared by the condensation of sodium *l*-methylbromosuccinate on potassium ethyldithiocarbamate in aqueous solution; it separates from water in long, pale yellow needles, m. p. 73—75° ($+1H_2O$), 107—109° (anhydrous), $[\alpha]_D$ −54·4° in alcoholic solution (for hydrated acid). The corresponding d-*isomeride* has m. p. 73—75°, $[\alpha]_D$ +55·5°, and is optically stable towards barium hydroxide solution at the ordinary temperature. The *r*-acid forms thin, colourless, anhydrous leaflets, m. p. 108—110°.

It has been shown by Holmberg (A., 1912, i. 131) that trithiocarbodiglycollic acid condenses with *r*-β-phenylethylamine to yield 3-β-phenylethylrhodanine; if the action is carried out with the optically active bases, however, the active diphenylethylthiocarbamides, needles, m. p. 195—197°, $[\alpha]_D$ −13·5° and +14·1° in alcoholic solution, are produced, identical with the products described by Lovén and Ohlsson (A., 1914, i. 830). The active 3-phenylethylrhodanines may, however, be prepared as follows. *d*-Phenylethylamine is treated successively with aqueous potassium hydroxide solution and carbon disulphide and with an aqueous solution of sodium chloroacetate, whereby d-*phenylethyldithiocarbamineglycollic acid*, colourless, crystalline powder, m. p. 101—102°, $[\alpha]_D$ +120·4° in alcoholic solution, is produced, which, when gently warmed with dilute acetic acid, loses water and passes into d-3-*phenylethylrhodanine*, pale yellow needles, m. p. 108—109°, $[\alpha]_D$ +301·2° in alcoholic solution. l-*Phenylethyldithiocarbaminecglycollic acid* has m. p. 101—102°, $[\alpha]_D$ −121·0° in alcohol, whilst l-3-*phenylethylrhodanine* has m. p. 108—109°, $[\alpha]_D$ −304·8°. The corresponding *r*-acid and *r*-rhodanine have m. p.'s 104—106° and 110—111° respectively. The latter is converted by a solution of sodium in alcohol into the *substance*. $CHMePh\cdot N\langle \begin{matrix} C(SH)(OEt) \\ | \\ CO-\!-CH_2 \end{matrix} \rangle S$, small, pale red prisms, m. p. 93—94°, which could only be isolated in one of two possible stereoisomeric forms.

r-3-*Ethylrhodanine*-5-*acetic acid*, small, pale yellow needles, m. p. 118—119°, is obtained by the action of potassium ethyldithiocarbamate on sodium *l*-bromosuccinate in aqueous solution, racemisation being complete. The *sodium hydrogen* salt, greenish-yellow plates, m. p. 242—243° (decomp.), is described.

The possibility of obtaining optically active products from salts of *l*-bromosuccinic acid and dithiocarbamates is established by experiments with diethyldithiocarbamates; when the substances are allowed to react in dilute aqueous solution, l-*diethyldithiocarbaminemalic acid*, $CO_2H\cdot CH_2\cdot CH(CO_2H)\cdot S\cdot CS\cdot NEt_2$, m. p. 106—107°, $[\alpha]_D$ −6·67° in alcohol, −40·9° in ethyl acetate, is obtained, which is probably not optically pure and is completely racemised in boil-

ing aqueous solutions. When the condensation is effected in more concentrated solution, complete racemisation occurs, and the corresponding *r*-acid, m. p. 114—116°, is formed, which is also produced by the action of *r*-bromosuccinic acid on potassium diethyldithiocarbamate.

Sodium *l*-β-bromosuccinamate condenses with potassium dimethyldithiocarbamate in aqueous solution to yield l-*dimethyldithiocarbamylsuccinamic acid*, colourless, silky needles, m. p. 158—159° (the sodium salt has $[\alpha]_D$ −4·2° in aqueous solution), which, in hot acid solution, passes into r-*dimethyldithiocarbamylsuccinic acid*, small, rhombic plates, m. p. 145—146°, and in alkaline solution is extensively decomposed with formation of the half-amide of fumaric acid. The acid is oxidised by permanganate to d-*dimethylthiocarbamylsuccinamic acid*, m. p. 148—149°, $[\alpha]_D$ +80·5° in alcoholic solution. r-*Dimethyldithiocarbamylsuccinamic acid*, small, colourless prisms, m. p. 162—163° (decomp.), is similarly prepared from *r*-β-iodosuccinamic acid, and is similarly oxidised to r-*dimethylthiocarbamylsuccinamic acid*, colourless prisms, m. p. 153—154° (decomp.). A similar series of reactions yields d-*phenylmethyldithiocarbamylsuccinamic acid*, small, colourless prisms, m. p. 164—165° (decomp.), $[\alpha]_D$ +11·0° in acetone (*ammonium* salt, colourless needles; *sodium* salt, small, colourless needles; *potassium* salt, colourless leaflets). The acid is converted into the r-*ester*, small, colourless, rhombic plates, m. p. 135—136°, by ethyl alcohol and hydrogen chloride. In hot acid solution it is transformed into r-*phenylmethyldithiocarbamylsuccinic acid*, m. p. 163—164°, and in alkaline solution it is extensively decomposed, yielding, amongst other products, the half-amide of fumaric acid. It is oxidised by permanganate to d-*phenylmethylthiocarbamylsuccinamic acid*, colourless, rhombic plates, m. p. 168° (decomp.), $[\alpha]_D$ +63·9° in alcohol. r-*Phenylmethyldithiocarbamylsuccinamic acid* forms colourless, rhombic plates, m. p. 157—158° (decomp.), and is oxidised to r-*phenylmethylthiocarbamylsuccinamic acid*, prisms, m. p. 160—161° (decomp.). H. W.

3 : 3′-Dimethyl-6 : 6′-di*iso*propylbenzidine. C. E. Andrews (U.S. Pat. 1314924).—Symmetrical dimethyldi*iso*propylbenzidine is produced by reducing crude mononitrocymene (such as may be obtained from "spruce turpentine") in alkaline solution to form hydrazocymene, subjecting the latter to the "benzidine transformation," and purifying the product by precipitation as sulphate. The sulphate is a white, crystalline powder which is easily separated by filtration, the impurities remaining in solution. The sulphate is decomposed on addition of a 10% sodium hydroxide solution, with liberation of the free base, dimethyldi*iso*propylbenzidine. The latter is an oily liquid, b. p. about 250°. It may be employed in the preparation of azo-dyes. Chemical Abstracts

Aromatic Analogues of Novocaine. Julius von Braun and Georg Kirschbaum (*Ber.*, 1919, **52**, [*B*], 2011—2015).—It has

recently been shown by Fränkel and Cornelius (A., 1919, i, 66) that derivatives of primary β-aminoethyl alcohol, in contrast to the tertiary *N*-dialkylated alkamine derivatives (stovaine, novocaine), do not possess anæsthetising action. The compounds which they have examined, however, contain an acyl residue attached to the nitrogen atom in place of the alkyl radicle of novocaine, and thus do not belong to quite the same type. Closer analogy is shown by a series of substances, which are now described, and in which a phenyl or substituted phenyl group is introduced in place of one of the alkyl groups. It is found that the aromatic substitution at the nitrogen atom of novocaine is without influence on its anæsthetising power if the basicity of the molecule is also suitably increased.

*N-β-Benzoyloxyethyl-*N*-methyl*-p-*phenylenediamine*, $NH_2 \cdot C_6H_4 \cdot NMe \cdot CH_2 \cdot CH_2 \cdot OBz$, long, slender needles, m. p. 56° (the *hydrochloride* and *acetyl* derivative, m. p. 152°, are described), is obtained by the reduction of the corresponding p-*nitroso*-derivative, pale green powder, m. p. 90°. Sodium *p*-nitrobenzoate reacts readily with β-chloro- or methyl-β-bromo-ethylaniline, yielding *N*-β-p-*nitrobenzoyloxyethyl-N-methylaniline*, $NMePh \cdot CH_2 \cdot CH_2 \cdot O \cdot CO \cdot C_6H_4 \cdot NO_2$, yellow needles, m. p. 70° (*hydrochloride*, colourless substance, *picrate*, m. p. 177°, *methiodide*, m. p. 144° [decomp.]), which is reduced to *N*-p-*aminobenzoyloxyethyl-N-methylaniline*, colourless leaflets, m. p. 112° (*acetyl* derivative, m. p. 132°). When the solution of the latter in dilute hydrochloric acid is treated with sodium nitrite, it yields the corresponding p-*nitroso*-derivative, m. p. 105—106°, which is almost quantitatively reduced by stannous chloride to *N-β-p-aminobenzoyloxyethyl-N-methyl-p-phenylenediamine*, $NH_2 \cdot C_6H_4 \cdot NMe \cdot CH_2 \cdot CH_2 \cdot O \cdot CO \cdot C_6H_4 \cdot NH_2$, m. p. 98°; the *hydrochloride* of the latter is freely soluble in water; the *diacetyl* derivative has m. p. 146°. Sodium 3:5-dinitrobenzoate and methylchloroethylaniline yield *N-β-3:5-dinitrobenzoyloxyethylmethylaniline*, m. p. 121°, which is normally reduced to the corresponding *diamino*-compound, m. p. 80°, the *hydrochloride* of which is very hygroscopic. H. W.

Action of Basic Reagents on Schiff's Bases. I. The Chloralnitroaniline Group. A. S. Wheeler and S. C. Smith (*J. Amer. Chem. Soc.*, 1919, **41**, 1862—1865).—Schiff's bases, obtained by condensing *o*- and *p*-nitroaniline with chloral (compare Wheeler and Weller, A., 1903, i, 246), yield hydroxy-, methoxy-, and ethoxy-derivatives with alcoholic potassium hydroxide, sodium methoxide, and sodium ethoxide; in each case, one chlorine atom is replaced. The *m*-nitroaniline–chloral product is so sensitive to these basic reagents that each of them in the cold breaks it up into its constituents. The nitro-group in the benzene ring of the amine stabilises the Schiff's bases to such an extent that basic reagents yield derivatives, although this is not true when it is in the meta-position. The following new substances are described: NN′-ββ*β-di-*

chlorohydroxyethylidenebis-o-nitroaniline, $OH\cdot CCl_2\cdot CH(NH\cdot C_6H_4\cdot NO_2)_2$, brilliant yellow prisms, m. p. 143°; *NN'-βββ-dichloromethoxyethylidenebis-o-nitroaniline*, yellow, rectangular plates, m. p. 147°; *NN'-βββ-dichloroethoxyethylidenebis-o-nitroaniline*, brilliant yellow, rectangular plates, m. p. 135°; *NN'-βββ-dichloroethoxyethylidenebis-p-nitroaniline*, bright yellow, fan-shaped crystals, m. p. 147°. H. W.

Constitution of Triphenylmethane Dyes. Hugo Kauffmann (*Ber.*, 1919, **52**, [*B*], 1421—1422).—One of the most puzzling facts in connexion with the constitution of triphenylmethane dyes is the hypsochromic effect of the introduction of a third amino-group in such compounds as malachite-green (Hantzsch, A., 1919, ii, 255). This can only be explained on electrochemical lines, as developed by the author in his theory of valency subdivision (this vol., i, 50). A compound containing two methoxyl auxochromes in the third benzene nucleus of malachite-green has now been obtained by converting Michler's ketone into the chloride with phosphoryl chloride and condensing this with *m*-dimethoxybenzene under the influence of aluminium chloride. *4:4'-Tetramethyldiamino-2'':4''-dimethoxytriphenylcarbinol* is white, has m. p. 195°, and dissolves in acids with the following colours: dilute acetic acid, bluish-green; dilute mineral acids, red becoming bluish-green on dilution; concentrated sulphuric acid, orange. J. C. W.

The Incompatibility of Calomel and Antipyrine. I. A New Mercury Compound of Antipyrine. Cesare Paderi (*Arch. farm. sperim. sci. aff.*, 1918, **26**, 359—380; from *Chem. Zentr.*, 1919, iii, 226—227).—Poisonous symptoms are observed particularly in children to whom these substances have been administered simultaneously or after a certain interval, but nothing is definitely known with regard to the mode of action. The author has therefore investigated the mutual behaviour of these substances under various conditions. Reaction does not occur in the presence of water or of acid media, such as gastric juice. In the presence of alkalis, however, changes occur which cause a marked toxicity; the product is not mercuric chloride, but a metallo-organic compound, the composition of which depends on the relative quantities of alkali and calomel. If sufficient of the former is present to combine with the whole of the chlorine, the compound,

$$Hg[NMe(OH):C_{10}H_9ON]_2,$$

obtained by Astre and Ville by the action of mercuric oxide on antipyrine, is obtained; otherwise, a *substance* is produced which gives the reactions of antipyrine, but contains one atom of mercury and one of chlorine to each molecule of antipyrine, and to which the formula $HgCl\cdot NMe(OH):C_{10}H_9ON$ is ascribed. Metallic mercury is also formed.

The new substance forms needles grouped in rosettes, m. p. 92°, and is sparingly soluble in cold water. It is more poisonous than

mercuric chloride. It gives precipitates with hydrogen sulphide or ammonium sulphide, and deposits mercury on copper; it does not react with sodium carbonate or potassium hydroxide, and only gives a slight precipitate with ammonia. With potassium ferrocyanide, it gives a flaky precipitate soluble in excess to a solution which slowly turns blue on exposure to air. Potassium iodide gives a turbid solution, from which a white precipitate, soluble in the warm or in excess of the reagent, slowly separates. A white precipitate is formed with stannous chloride, which disappears on shaking. Gold chloride gives a yellow precipitate, which is reduced when warmed. The substance also shows the antipyrine reactions with ferric chloride and with nitrous acid. H. W.

Reaction of the Potassium Salts of 2-Thiol-5-thio-4-phenyl-4 : 5-dihydro-1 : 3 : 4-thiodiazole and 2 : 5-Dithiol-1 : 3 : 4-thiodiazole with Halogenated Organic Compounds. (Sir) Prafulla Chandra Ray, Prafulla Chandra Guha, and Radha Kishen Das (T., 1919, **115**, 1308—1312).

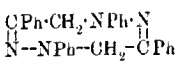
Photochemical Transformations in the Triphenylmethane Series. I. Lifschitz [with Ch. L. Joffé] (*Ber.*, 1919, 52, [*B*], 1919—1926).—When triphenylmethane dyes are mixed with potassium cyanide, they change into colourless triarylacetonitriles (Hantzsch, A., 1900, i, 256; Müller, A., 1910, i, 868). It is now shown that these colourless nitriles are rearranged into the coloured triphenylmethane cyanides when exposed to the light of an iron arc in methyl- or ethyl-alcoholic solutions in quartz vessels, as, for example, in the *p*-rosaniline series, $(NH_2{\cdot}C_6H_4)_3C{\cdot}CN \longrightarrow [(NH_2{\cdot}C_6H_4)_3{:}C]CN$. Solvents like benzene, ether, and chloroform have no effect, because of their small dissociating power, but solutions in dilute mineral acids also remain colourless (provided that the nitrile is pure), the explanation in this case being that the selective absorption of the necessary long-wave ultra-violet light is prevented by the participation of the amino-groups in salt formation. Further evidence of the production of the ionisable salts is the fact that the electrical conductivity of the alcoholic solutions increases on exposing them to the light. The experimental evidence (absorption curves, etc.) is based on the cases of pararosaniline and crystal-violet. J. C. W.

Oxidation of the Hydramides. J. Bougault and P. Robin (*Compt. rend.*, 1919, **169**, 978—980).—The three hydramides examined, benzhydramide, anishydramide, and piperonhydramide, on oxidation with iodine and sodium carbonate, all gave a 30—40% yield of the corresponding cyanidine. These cyanidines were subjected to hydrolysis with hydrochloric acid in acetic acid solution at a temperature not exceeding 120°. Under these conditions, triphenylcyanidine gave benzoic acid, ammonia, and benzamidine. Trimethoxyphenylcyanidine, $(OMe{\cdot}C_6H_4{\cdot}CN)_3$, and trimethylene-

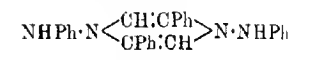
dioxyphenylcyanidine, $(CH_2{:}O_2{:}C_6H_3{\cdot}CN)_3$, gave results of the same order.

Hydrocinnamide when oxidised by iodine and sodium carbonate did not give the corresponding cyanidine, but only an amorphous resin. The author considers that this result supports Delépine's view that hydrocinnamide is really a glyoxalidine. W. G.

Action of Hydrazines on α-Chloro-ketones, and the Constitution of the so-called Tetraphenyltetracarbazone. Sven Bodforss (*Ber.*, 1919, **52**, [*B*], 1762—1775).—In 1886, Hess obtained a yellow compound, m. p. 137°, by the action of phenylhydrazine on ω-bromoacetophenone in ice-cold alcohol, and assigned to it the formula $NPh\langle{}^{---N}_{CH_2}\rangle CPh$. This substance has been investigated by Culmann (A., 1890, 1268), who proposed a doubled formula, $C_{28}H_{24}N_4$, from very erroneous arguments, and the constitution of a tetraphenyltetracarbazone; Bender (A., 1888, 53, 1188); and Freer (A., 1899, 358); and recently Scholtz (A., 1918, i, 96), obtained a colourless compound, m. p. 174°, by condensing the agents in boiling alcohol, which he regarded as tetraphenyl-β-tetracarbazone (I), that is, as an isomeride of Hess's compound. From an analogy with the action of ammonia on ω-bromoacetophenone, which results in the formation of pyrazines (Tutin and Caton, T., 1910, **97**, 2495), it is more than likely that Scholtz's compound is 1:4-dianilino-2:5-diphenylpyrazine (II) or the -2:6-isomeride.



(I.)



(II.)

In order, in the first place, to get a correct idea of the molecular formula for Hess's compound, the author condensed ω-*p*-dichloroacetophenone with phenylhydrazine under the same conditions, and obtained a product of the empirical formula $C_{14}H_{11}N_2Cl$. This confirms $C_{14}H_{12}N_2$ as the simplest formula for Hess's compound, and as the molecular weight in boiling benzene is a little more than 200, this is also the molecular formula. Various alternative structural formulæ are critically examined, and arguments are advanced in favour of Hess's original suggestion. The substance should therefore be designated 1:3-*diphenyl*-Δ^2-1:2-*diazene*.

The product given by phenylhydrazine and ω-*p*-dichloroacetophenone is, consequently, 1-*phenyl*-3-p-*chlorophenyl*-Δ^2-1:2-*diazene*, $NPh\langle{}^{---N}_{CH_2}\rangle C{\cdot}C_6H_4Cl$; it crystallises in felted masses of thin, yellow needles, m. p. 164—164·5°. ω-Bromoacetophenone and *p*-bromophenylhydrazine yield 3-*phenyl*-1-p-*bromophenyl*-Δ^2-1:2-*diazene*, orange, glistening needles, m. p. 165° (decomp.), that is, a substance quite distinct from Freer's azo-compound, formed according to the scheme: $C_6H_5{\cdot}COMe + NH_2{\cdot}NH{\cdot}C_6H_4Br \rightarrow C_6H_4Br{\cdot}NH{\cdot}N{:}CPhMe \rightarrow C_6H_4Br{\cdot}NH{\cdot}NH{\cdot}CPh{:}CH_2 \xrightarrow{air} \rightarrow$

$C_6H_4Br\cdot N{:}N\cdot CPh{:}CH_2$, with which it should be identical if Freer's interpretation of Hess's reaction is correct; thus,

$$C_6H_5\cdot CO\cdot CH_2Br + NH_2\cdot NH\cdot C_6H_4Br \longrightarrow$$
$$C_6H_4Br\cdot NH\cdot N{:}CPh\cdot CH_2Br \longrightarrow C_6H_4Br\cdot NH\cdot NH\cdot CPh{:}CHBr \xrightarrow{-HBr}$$
$$C_6H_4Br\cdot N{:}N\cdot CPh{:}CH_2.$$

Phenylhydrazine and *p*-chloroacetylanisole yield 1-*phenyl*-3-*p*-*anisyl*-Δ^2-1:2-*diazene*, yellow, felted needles, m. p. 141° (decomp.).

When Hess's compound is treated with acids (best, alcoholic hydrogen chloride in the cold), it yields a compound, $C_{22}H_{18}N_2$, which Culmann regarded as a phenylhydrazine derivative of diphenacyl, since he obtained diphenacyl from it on boiling with 30% sulphuric acid. Freer, however, considered it to be the phenylhydrazone of deoxybenzoin. It is now found that Culmann was correct, for the compound (white needles, m. p. 114°) may be prepared by condensing diphenacyl with phenylhydrazine. The formation of this 1:3:6-*triphenyl*-1:4-*dihydropyridazine* from the diazene is explained in this way:

$$2\ \begin{matrix} CPh\cdot CH_2 \\ \| \quad | \\ N\text{—}NPh \end{matrix} \longrightarrow \begin{matrix} CPh\cdot CH{:}CH\cdot CPh \\ \| \qquad\qquad \| \\ N\cdot NHPh \qquad N\cdot NHPh \end{matrix}$$

$$\xrightarrow{-NH_2\cdot NHPh} \begin{matrix} CPh{:}CH\cdot CH_2\cdot CPh \\ | \qquad\qquad\quad \| \\ NPh\text{———}N \end{matrix}.$$

Phenylmethylhydrazine condenses with ω-bromoacetophenone to form the phenylmethylosazone of phenylglyoxal, orange needles, m. p. 152° (Culmann). The same product is obtained by heating phenylmethylhydrazine with phenacylanilide, but in another *modification*, thin, orange-red, shimmering leaflets, m. p. 153—154°.

The reaction between chloroacetone and phenylhydrazine at low temperatures was described by Bender. The product is purified by crystallisation from methyl alcohol, whereby the m. p. is raised from 158° to 162·5°, and its properties suggest that it is the *phenylhydrazone* of *phenylhydrazinoacetone*.

$$NHPh\cdot NH\cdot CH_2\cdot CMe{:}N\cdot NHPh.$$

For example, it is oxidised by nitrous acid to methylglyoxalosotetrazone (von Pechmann, A., 1888, 1288). J. C. W.

The Coupling of Diazo-compounds with Hydrocarbons. Kurt H. Meyer (*Ber.*, 1919, **52**, [*B*]. 1468—1476).—In the majority of cases, the first step in the coupling of a compound with a diazonium salt is supposed by the author to be addition at double linkings (A., 1914, i, 882), but Karrer holds the opinion that addition at the amino-, hydroxy-, or alkyloxy-group represents the initial stage (A., 1915, i, 1073). It is now shown that certain unsaturated hydrocarbons can couple with suitable diazo-compounds, forming typical azo-derivatives, which indicates that, whilst Karrer's hypothesis may undoubtedly be correct in certain cases, addition at double bonds plays the principal rôle.

[With VIKTOR SCHOELLER.]—Butadiene couples with diazotised 2:4-dinitroaniline in glacial acetic acid to form *α-2:4-dinitrophenylazo-Δ^{αγ}-butadiene*, $CH_2{:}CH{\cdot}CH{:}CH{\cdot}N{:}N{\cdot}C_6H_3(NO_2)_2$, in brilliant yellow needles, m. p. 111° (decomp.). Piperylene couples with the nitrobenzenediazonium chloride to form *p-nitrophenylazopiperylene*, $C_{11}H_{11}O_2N_3$, glistening, yellow needles, m. p. 137°, and *2:4-dinitrophenylazopiperylene*, $C_{11}H_{10}O_4N_4$, orange-yellow crystals, which darken at 105° and have m. p. 131° (decomp.). Isoprene forms *2:4-dinitrophenylazoisoprene*,

$$C_{11}H_{10}O_4N_4,$$

orange-yellow crystals, m. p. 98° (decomp.). The best results are obtained with *βγ*-dimethyl-Δ^{αγ}-butadiene, and it is rather suggestive that a methyl group in the *β*-position should have this favourable influence, for *m*-cresol methyl ether couples more readily than anisole (Auwers and Michaelis, A., 1914, i, 744). *α-p-Nitrophenylazo-βγ-dimethyl-Δ^{αγ}-butadiene*,

$$CH_2{:}CMe{\cdot}CMe{:}CH{\cdot}N_2{\cdot}C_6H_4{\cdot}NO_2,$$

forms long, yellow needles, m. p. 177°, gives an *additive* compound with mercuric chloride, brilliant red needles, decomp. 109°, a dark violet compound with stannic chloride, and a *tetrabromide*, $C_{12}H_{13}O_2N_3Br_4$, dull orange, microscopic needles, m. p. 132° (decomp.), and may be reduced by means of tin and hydrochloric acid to *α-p-aminophenylhydrazo-βγ-dimethyl-Δ^{αγ}-butadiene*,

$$CH_2{:}CMe{\cdot}CMe{:}CH{\cdot}N_2H_2{\cdot}C_6H_4{\cdot}NH_2,$$

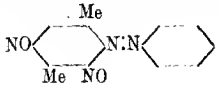
a pale greenish-yellow base, m. p. 125° (decomp.), which is very easily oxidised on exposure to air. *α-2:4-Dinitrophenylazo-βγ-dimethyl-Δ^{αγ}-butadiene* crystallises in bundles of slender prisms, decomp. 126°. J. C. W.

Aromatic Nitro-derivatives. VIII. Action of Phenylhydrazine on Trinitro-*p*-xylene and on Ethers of Trinitro-*m*-cresol. M. GIUA (*Gazzetta*, 1919, **49**, ii., 146—152. Compare A., 1918, i. 552).—Since trinitro-*p*-xylene contains a nitro-group which is readily replaceable, the action on it of phenylhydrazine should yield 3:5-dinitro-2-benzenehydrazo-*p*-xylene. Although formation of the latter in the first phase of the reaction may be assumed, it is found that the reaction proceeds further, reduction of a nitro-group and simultaneous elimination of a molecule of water from the ·NH·NH· group and another nitro-group in the ortho-position to it resulting in the formation of a 3:5-dinitroso-2-benzeneazo-*p*-xylene as final product; this is accompanied by 3-nitro-5-nitroso-2-benzenehydrazo-*p*-2-xylene, which represents an intermediate product.

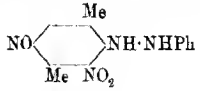
The methyl and ethyl ethers of trinitro-*m*-cresol react in the same way as trinitroanisole (compare Giua and Cherchi, succeeding abstract) with phenylhydrazine, the alkyloxy-group being replaced by the phenylhydrazine residue, with formation of 3-benzenehydrazotrinitrotolnene. The latter is, however, so unstable that when heated to boiling with alcohol it is transformed immediately into 3-benzeneazonitrodinitrosotoluene; during this change, the alcohol is converted into aldehyde, the second nitro-

group in the ortho-position to the hydrazo-group being reduced and a molecule of water simultaneously eliminated from the hydrazo-group and the other nitro-group.

3:5-*Dinitroso-2-benzeneazo*-p-*xylene* (I) forms shining, yellow



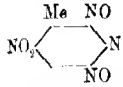
(I.)



(II.)

plates, m. p. 185°, and yields a dark coloration when heated with potassium hydroxide in alcoholic solution.

3-*Nitro-5-nitroso-2-benzenehydrazo*-p-*xylene* (II) forms shining, red, prismatic plates melting at 145° to a red oil, which readily decomposes if the heating is prolonged. With alkali and alcohol in the hot, it gives a deep red coloration, and when heated in presence of alcohol it is converted into the preceding compound.

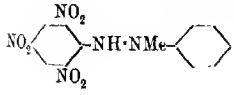


6-*Nitro*-2 : 4-*dinitroso*-3-*benzeneazotoluene* (annexed formula) forms pale yellow, silky needles, m. p. 148—149°. Under the influence of light it becomes brownish-yellow, and with alkali in alcoholic solution it produces a reddish-brown coloration.

T. H. P.

Aromatic Nitro-compounds. IX. Behaviour of Trinitroanisole. M. Giua and F. Cherchi (*Gazzetta*, 1919, **49**, ii, 152—157).—According to Masland and Sparre (A., 1913, i. 853), trinitroanisole is hydrolysed, even in the cold, by solutions of alkali carbonates, with formation of picrates, and to some extent by water in the hot, with formation of methyl alcohol and picric acid, whilst cold water exerts only slight hydrolysing action. The authors regard this so-called hydrolysis as a process of substitution in the methoxy-group; this group is easily replaceable, even by radicles of organic bases, in consequence of the ortho-para-influence of the nitro-groups present in the molecule.

Trinitroanisole may be used with advantage to replace picryl chloride in many organic syntheses. Thus, with hydrazine hydrate it gives 2:4:6-trinitrophenylhydrazine; with phenylhydrazine, either trinitrohydrazobenzene or nitrodinitrosoazobenzene, according to the temperature, and with aniline, trinitrodiphenylamine, from which hexanitrodiphenylamine may be obtained by further nitration. The conditions necessary for all these reactions have been determined.

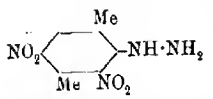


The action of *as*-phenylmethylhydrazine on trinitroanisole yields 2 : 4 : 6-*trinitro*-N′-*methylhydrazobenzene* (annexed formula), which crystallises in reddish-yellow or intense garnet-red prisms (probably

isomeric), m. p. 153°, and dissolves in concentrated sulphuric acid with a dark red coloration, and in alkali with a dark green coloration. T. H. P.

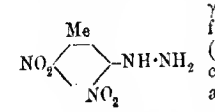
Aromatic Nitro-derivatives. XI. Action of Hydrazine Hydrate on Aromatic Nitro-compounds. M. Giua (*Gazzetta*, 1919, **49**, ii, 166—175).—The action of hydrazine hydrate on various aromatic nitro-derivatives containing a labile nitro-group has been investigated. With trinitro-*p*-xylene and β- and γ-trinitrotoluenes, the reaction occurs readily in alcoholic solution, the labile nitro-group being replaced by the hydrazine residue. With the methyl ether of trinitro-*m*-cresol under the same conditions, the ortho-para-influence exerted by the nitro-groups on the methoxy-group brings about replacement of the latter by the hydrazine residue.

3:5-*Dinitro*-p-2-*xylylhydrazine* (annexed formula), prepared from trinitro-*p*-xylene and hydrazine hydrate,



forms yellow prisms, m. p. 180° (decomp.), and with alkalis, in either alcoholic or acetone solution, gives a brick-red coloration. Its β-*acetyl* derivative, $C_6HMe_2(NO_2)_2\cdot NH\cdot NHAc$, forms pale yellow, shining plates, m. p. 232° (decomp.), and gives a dark red coloration with alkalis in alcoholic solution. The β-*benzylidene* derivative, $C_6HMe_2(NO_2)_2\cdot NH\cdot N:CHPh$, forms long, pale yellow needles, m. p. 221° (decomp.), and dissolves in potassium hydroxide to an intense violet-red solution. The β-*anisylidene* derivative, $C_{16}H_{16}O_5N_4$, crystallises in slender, golden-yellow needles, m. p. 224° (decomp.), and yields an intense carmine-red coloration with potassium hydroxide.

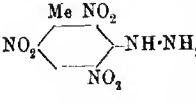
4:6-*Dinitro*-m-*tolylhydrazine* (annexed formula), prepared from γ-trinitrotoluene and hydrazine hydrate,



forms reddish-yellow crystals, m. p. 194° (decomp.), its alcoholic solution being coloured intensely red by addition of an alkali.

The action of hydrazine hydrate on β-trinitrotoluene in alcoholic solution yields a *compound* which contains 28·31—28·7% N, and crystallises in golden-yellow prisms, m. p. 150° (decomp.); it may possibly be an aziminole derivative of the formula $NO_2\cdot C_6H_2Me\langle\begin{matrix}N\\ N(OH)\end{matrix}\rangle N$.

2:4:6-*Trinitro*-m-*tolylhydrazine* (annexed formula), prepared by the action of hydrazine hydrate on the methyl ether of trinitro-*m*-cresol (m. p. 94°; Larter, P., 1901, 183, gave m. p. 91°) (compare this vol., i, 19), crystallises in shining, golden-yellow plates, m. p. 176° (gas evolution), and dissolves in alkali solution, giving a brownish-red coloration. The β-*acetyl*



derivative, $C_9H_9O_7N_5$, forms large, yellow prisms, m. p. 136°, and gives a red coloration with alkali in alcoholic solution. The *αβ-diacetyl* derivative, $C_6HMe(NO_2)_3{\cdot}NAc{\cdot}NHAc$, crystallises in nacreous plates, m. p. 216° (decomp.), and gives a dark red coloration with alkali in alcoholic solution. The *benzylidene* derivative, $C_{14}H_{11}O_6N_5$, forms small, reddish-yellow prisms, m. p. 249—250° (decomp.), burns with difficulty, leaving considerable carbonaceous residue, and dissolves in alkali solutions, giving an intense brick-red coloration. T. H. P.

The Proteolytic Activity of Pancreatic Amylase Preparations. H. C. Sherman and Dora E. Neun (*J. Amer. Chem. Soc.*, 1919, **41**, 1855—1862).—The experiments were undertaken with a view to throwing some further light on the nature of the relationship which exists between the amylolytic and proteolytic activities of purified pancreatic amylase preparations. High-grade commercial pancreatin was purified as described previously (Sherman and Schlesinger, A., 1912, i, 815; 1915, i, 604; Sherman and Neun, A., 1918, i, 414), except that in the final precipitation the usual 1:1 alcohol–ether mixture was replaced by a 2:1 mixture. A precipitate (*A*) is thus obtained, after removal of which a second precipitate (*B*) is isolated by adding more ether to the filtrate. The amylolytic activity of *A* is found to be lower than that of *B*, but the latter was more active than the usual amylase preparations; the proteolytic activity was higher in precipitate *A* than in precipitate *B*. Interpretation of the results is rendered difficult by the exceedingly unstable nature of the material under purification and the impossibility of pushing the fractionation further, because of the great tendency to loss of amylolytic activity when pancreatic amylase in the absence of salts and carbohydrates is held in solution or subjected to precipitation. On the whole, it seems probable that a partial separation of a mixture of amylase and protease was accomplished, but that amylolytic activity was partly lost because of the extra manipulation, since amylolytic activity deteriorates much more rapidly than proteolytic, at least under conditions such as obtained in these experiments. The further possibility that there are enzymo particles which have both amylolytic and proteolytic activities is not excluded. H. W.

Influence of Aspartic Acid and Asparagine on the Enzymic Hydrolysis of Starch. H. C. Sherman and Florence Walker (*J. Amer. Chem. Soc.*, 1919, **41**, 1866—1873. Compare Sherman, Walker, and Caldwell, A., 1919, i, 559).—The action of saliva, pancreatin, and purified pancreatic amylase on alkali-washed potato, wheat, maize, and rice starches, and on "Lintner" soluble starch, is accelerated by the addition of small amounts of boiled, neutralised water extract of potato, whilst the action of the vegetable amylases tested was not influenced by the addition of potato extract.

The addition of neutralised aspartic acid or asparagine accelerated

the action of saliva, pancreatin, and purified pancreatic and malt amylases. Clear evidence of activation was not obtained in the case of malt extract or of the preparations made from *Aspergillus oryzae*.

The addition of both sodium aspartate and asparagine to the same digestion mixture produces practically the same activation as does one of these substances alone. Thus the activating effects of the substances are interchangeable rather than additive. Activation is not due in these experiments to change in hydrogen-ion concentration or merely to a more favourable concentration of electrolyte. The amino-compounds to be tested were added to a substrate which already contained the optimum concentrations of sodium chloride and phosphate, the reported activation being thus additional to the activity induced by chloride and phosphate. Moreover, sodium aspartate is not interchangeable with sodium chloride in the activation of purified pancreatic amylase. The effects of other amino-acids are being studied similarly. H. W.

The Separation of Potato Tyrosinase into Components. Hugo Haehn (*Ber.*, 1919, **52**, [*B*], 2029—2041).—Potato tyrosinase can be separated by filtration into a thermolabile residue (α-tyrosinase) and a filtrate (activator), which is stable towards heat; when separately tested, neither component shows the tyrosine reaction, but the mixture of the two is again active. The inactive residue can be activated by the addition of the solution obtained by boiling expressed potato juice in dilute acetic acid solution, and subsequent filtration, as also by the addition of an aqueous solution of the ash obtained by igniting the residue left on the evaporation of such a solution.

Toluene appears to act as an oxygen carrier; it is found that preservation of solutions beneath toluene does not inhibit the enzymic process of tyrosinase, as would be expected in consequence of the assumed exclusion of air. Further, it is shown that the alkaline solutions of pyrogallol become brown even when preserved beneath a layer of toluene which is 8 cm. high. The result is not due to hydroclastic activity of toluene, since the pyrogallol solutions remain unchanged when the experiment is performed in an atmosphere of hydrogen. H. W.

Urease and the Radiation Theory of Enzyme Action. III. H. P. Barendrecht (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 29—45. Compare A., 1919, i, 604).—A continuation of previous work. From electrometric measurements of the hydrogen-ion concentration of phosphate solutions to which 8% of carbamide had been added, it is shown that the dissociation of water is decreased. The study of the urease action on carbamide was continued in solutions containing 5% of alcohol; all other conditions were the same as in the preceding experiments. It is shown that k_w is decreased from $10^{-13\cdot78}$ to $10^{-13\cdot98}$ by this addition, and the constant m for the hydrolysis of carbamide is reduced from 0·00381

to 0·00335. The influence of enzyme concentration is also studied. The results indicate that above a definite concentration of urease the activity is constant, but below this value the activity decreases.
J. F. S.

Course of the Degradation of Urea by Urease. H. von Euler and G. Brandting (*Biochem. Zeitsch.*, 1919, **97**, 113—123).—Urease preparations previously kept at 17·5°, 30°, 35°, 40°, 45°, and 50° respectively for some days have shown constant activity. The authors cannot therefore confirm the periodicity in the activity of urease observed by Groll (A., 1919, i, 425). Groll's results are discussed. S. S. Z.

Biochemistry of the Enzyme of Soja Beans (Urease). D. H. Wester (*Chem. Weekblad*, 1919, **16**, 1442—1454).—A continuation of the author's previous research (A., 1916, ii, 502). The urease content of a solution, if not too dilute, may be estimated from the amount of urea which has undergone conversion. Neither the concentration of the urea solution nor the conversion products obtained affect the action of the enzyme. Urease solution retains its activity after prolonged storage, but it is necessary, on the other hand, to use freshly made urea solutions. For extracting the urease from the soja beans, glycerol to the extent of 50% may be added to the solution with advantage, but increased amounts will reduce the proportion of urease, and, further, the addition of glycerol to the mixture of urease and urea retards the enzymic process. The author finds that in some respects extract of Canavalia beans acts similarly to that of soja beans, but this investigation is still incomplete. W. J. W.

A Peculiarity of the Enzymic Action of Soja-bean Extract at 37°. D. H. Wester (*Chem. Weekblad*, 1919, **16**, 1461—1463).—Heating the extract for three days at 37° was found to reduce its efficiency, but heating for longer periods did not reduce the enzymic action proportionately. The following results were obtained:

	Hours.	Days.				
		7	14	21	28	35
Time	3					
Urea equivalent	126	47	38·2	90	85	60·3

The curve representing the above results is therefore a zigzag.
W. J. W.

Action of Urease at 35°. J. Temminck Groll (*Chem. Weekblad*, 1919, **16**, 1527).—The author confirms Wester's investigations (preceding abstract). He states that this behaviour is not a characteristic of one particular preparation, but is an actual property of urease and probably also of other ferments, such as lipases and ptyalin. W. J. W.

The Action of Neutral Salts on the Osmotic Pressure and other Qualities of Gelatin. Jacques Loeb (*Proc. Soc. Biol. Med.*, 1918, **15**, 129–131).—According to the author's hypothesis, neutral salts act on proteins, which, like gelatin, are stronger acids than bases, by forming metal proteinates. The anion either does not enter into combination at all with the gelatin or enters into a combination where its influence on the protein is not felt. When gelatin has been previously treated with an acid, for example, hydrochloric acid, gelatin chloride or hydrochloride is formed, which dissociates into a positive gelatin ion and a negative chlorine ion. Neutral salts act on such gelatin chloride by exchanging their anion for the protein. This explains why the increase in the osmotic pressure and the viscosity, and the swelling of gelatin caused by the salt, do not become noticeable unless the excess of salt is washed away, since the presence of the salt represses the electrolytic dissociation of the gelatin salt formed.

Chemical Abstracts.

New Organic Compounds of Phosphorus. H. Staudinger and Jules Meyer (*Helv. Chim. Acta*, 1919, **2**, 612–618).—Previous attempts to obtain a compound in which a nitrogen atom is directly united to five carbon atoms having proved unsuccessful (this vol., i. 34), the authors have turned their attention to the preparation of a similar compound from phosphorus, since, in general, this element shows a greater tendency to pass into the quinquevalent condition than does nitrogen.

Attempts to prepare phosphorus pentaethyl from tetraethylphosphonium iodide and zinc ethyl did not give the desired result, since action did not occur at low temperatures, whilst at 150° the products were butane and an additive product of triethylphosphine and zinc iodide. Triethylphosphine did not react with zinc ethyl or with magnesium ethyl bromide, whilst a phosphine-methylene derivative could not be prepared from triethylphosphine oxide and diphenylketen. The latter, however, unites readily with triethylphosphine (but not with triphenylphosphine) in absolute ethereal solution, yielding the unstable, pale yellow, crystalline additive *product*, $Et_3P<^{O}_{C:CPh_2}$, which sinters at 80° and is completely decomposed at 100°. When heated, it dissociates into triethylphosphine and diphenylketen, and a similar phenomenon is observed when it is dissolved in benzene. It is decomposed by water into triethylphosphine and diphenylacetic acid.

Hofman has shown that triethylphosphine combines readily with carbon disulphide, and has formulated the product as a derivative of carbamide; since, however, it shows the closest analogy to the keten additive compound, the authors assign to it the structure $Et_3P<^{S}_{C:S}$, which has previously been suggested by Jacobson (*Lehrbuch org. Chemie*, i, 427). When gently heated, it dissociates into carbon disulphide and triethylphosphine, whilst at a higher

temperature it yields triethylphosphine sulphide (the simultaneous formation of carbon monosulphide could not be established). The additive compound of triethylphosphine and phenylthiocarbimide is dissociated by gentle heating.

Carbodiphenyldi-imide does not react with triethylphosphine.

H. W.

New Organic Compounds of Phosphorus. II. Phosphazines. H. Staudinger and Jules Meyer (*Helv. Chim. Acta*, 1919, **2**, 619—635).—Tertiary phosphines combine more or less readily with the most varied aliphatic diazo-compounds, yielding derivatives, for which the name phosphazines is proposed, in accordance with the scheme $CR_2{:}N{:}N + PR_3 \longrightarrow R_2C{:}N{-}N{:}PR_3$. They are decomposed by water into the hydrazone and phosphine oxide. When heated, they lose nitrogen, but the exact course of the reaction has only been followed in the case of triphenylphosphinebenzophenoneazine, when triphenylphosphinediphenylmethylene is produced (compare preceding abstract). They have more or less strongly marked basic properties and unite with two molecules of a monobasic acid to form salts, the constitution of which is not definitely established.

Triethylphosphinefluorenoneazine, $PEt_3{:}N{\cdot}N{:}C{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}$, golden-yellow, rather unstable crystals, m. p. 160°, is prepared by the action of diazofluorene on triethylphosphine in benzene solution in an atmosphere of nitrogen. With methyl iodide, it yields the *product*, $C_{19}H_{23}N_2P,CH_3I$, pale yellow powder, m. p. 109—113°. It dissolves in dilute sulphuric and hydrochloric acids, and is recovered unchanged when the acid is neutralised; with the concentrated acids, it yields deep orange solutions, which become colourless on dilution with water. The yellow, crystalline *hydrochloride* is described. When hydrolysed with aqueous alcohol, it yields fluorenonehydrazine and triethylphosphine oxide, whilst with moist chloroform it yields *bisdiphenylenetetrahydrotetrazine* (?), orange-coloured crystals, m. p. about 325°.

Triphenylphosphinefluorenoneazine forms comparatively stable, compact, yellow crystals, m. p. 209—210° (decomp.). It is much more feebly basic than the triethylphosphine derivative, and neither unites with methyl iodide nor dissolves in dilute aqueous acids. The *hydrochloride* is an unstable substance which slowly loses hydrogen chloride when preserved; it softens at about 193°, but has not a definite m. p. *Phenyldiethylphosphinefluorenoneazine* is readily obtained in stable, yellow crystals, m. p. 115°, which are hydrolysed to fluorenehydrazone and phenyldiethylphosphine oxide, and is feebly basic in character; the *hydrochloride*, pale yellow crystals, m. p. above 250° (indefinite), is described.

Diphenyldiazomethane reacts very readily with triethylphosphine, but the product, *triethylphosphinebenzophenoneazine*,

$$PEt_3{:}N{\cdot}N{:}CPh_2,$$

is so unstable that it could not be isolated in the pure state; its

formation is inferred from the fact that benzophenonehydrazine is obtained by the immediate treatment of the crude product with alcohol. When preserved, it readily yields *bisdiphenyltetrahydrotetrazine*, pale yellow, crystalline powder, m. p. 204·5—205·5°. *Phenyldiethylphosphinebenzophenoneazine*, $PEtPh{\cdot}N{\cdot}N{:}CPh_2$, forms pale yellow crystals, m. p. 113°, and is hydrolysed to benzophenonehydrazone and phenyldiethylphosphine oxide. It dissolves in aqueous acids. *Triphenylphosphinebenzophenoneazine*, $PPh_3{:}N{\cdot}N{:}CPh_2$, is an almost colourless, stable, crystalline powder, m. p. 173° (decomp.). It is slowly hydrolysed to benzophenonehydrazone and triphenylphosphine oxide. It is scarcely affected by dilute acids. The colourless *hydrochloride* is a crystalline powder, m. p. ca. 185° (decomp.).

Triethylphosphine and phenyldiethylphosphine react with ethyl diazoacetate, but crystalline products could not be isolated; triphenylphosphine, on the other hand, yields *ethyl triphenylphosphineglyoxylate-azine*, $PPh_3{:}N{\cdot}N{:}CH{\cdot}CO_2Et$, colourless crystals, m. p. 113—114°.

Benzoylphenyldiazomethane reacts readily with triethylphosphine and triphenylphosphine. Benzoyldiazoacetic ester also reacts with both phosphines, yielding azines, which will be described subsequently.

The tervalent phosphorus atom of phosphorus phenyl dichloride and of phosphorus trichloride appears unable to undergo these additive reactions. H. W.

New Organic Compounds of Phosphorus. III. Phosphinemethylene Derivatives and Phosphineimines. II. Staudinger and Jules Meyer (*Helv. Chim. Acta*, 1919, **2**, 635—646).—An account is given of the preparation and properties of two new classes of derivatives, namely, triphenylphosphinediphenylmethylene, obtained by loss of nitrogen from triphenylphosphinebenzophenoneazine, as indicated in the preceding abstract, and phosphineimine compounds, produced by addition of azides to phosphines and spontaneous decomposition of the phosphazides primarily formed: $NPh{:}N{\cdot}N{:}PPh_3 \longrightarrow NPh{:}N{\cdot}N{:}PPh_3 \longrightarrow NPh{:}PPh_3$.

Triphenylphosphinediphenylmethylene, $PPh_3{:}CPh_2$, m. p. 170—172°, is best prepared by heating the corresponding azine in small quantities at a time in a vacuum at 185—195°. It crystallises from benzene in red leaflets, which contain approximately one molecule of benzene, which is only eliminated with difficulty. It dissolves in warm dilute hydrochloric acid, forming a colourless solution, from which *triphenylbenzhydrylphosphonium chloride*, colourless needles, m. p. 240—242°, separates on cooling. When heated with a solution of sulphur in carbon disulphide, it forms thiobenzophenone and triphenylphosphine sulphide. It does not react with carbon disulphide, benzylideneaniline, dimethylaminobenzaldehyde, thiobenzophenone, or with diphenylketen. It

appears, therefore, to be considerably less reactive than diphenylketen, and its inability to unite with the latter is somewhat remarkable, more particularly since it is capable of reacting with phenylcarbimide to yield *diphenylketenphenylimine*.

Triphenylphosphinephenylimine, PPh_3:NPh, forms a pale yellow, crystalline powder or large plates, m. p. 131—132°, and is best prepared by the action of triphenylphosphine on phenylazide in absolute ethereal solution. It has feebly basic properties and dissolves to some extent in dilute sulphuric and hydrochloric acids; the boiling acids hydrolyse it to triphenylphosphine oxide and the aniline salt. It does not unite with substances containing a single double bond, such as benzaldehyde, benzylideneaniline, or thiobenzophenone. Reaction readily occurs, however, with compounds containing paired double linkings; thus, dry carbon dioxide at 130—140° converts it into triphenylphosphine oxide and phenylcarbimide, whilst triphenylphosphine sulphide and phenylthiocarbimide are formed with carbon disulphide. Triphenylphosphine oxide and triphenylphosphine sulphide are similarly obtained when it is gently warmed with phenylcarbimide and phenylthiocarbimide respectively. *Triphenylphosphine-p-tolylimine* forms pale yellow crystals, m. p. 134—135°, and is decomposed by carbon dioxide or carbon disulphide in the same manner as the phenylimine. *Triphenylphosphine-m-xylylimine* has m. p. 130—131°.

Phosphorus trichloride and phosphorus phenyl dichloride do not react with phenylazide.

Phenyldiethylphosphine and triethylphosphine in the undiluted condition react explosively with phenylazide. By conducting the action between the latter substances in the presence of absolute ether, it was found possible to isolate a crystalline *product*, golden-yellow leaflets, m. p. 68·5—69·5°, which was too unstable to permit further purification, but appears to have a nitrogen content higher even than that required for the phosphazide; triethylphosphine oxide was isolated from the ethereal mother liquor. H. W.

Aromatic Arsenic Compounds. I. Plan of Procedure for the Synthesis of Arsenicals for Chemotherapeutic Research. Walter A. Jacobs and Michael Heidelberger (*J. Amer. Chem. Soc.*, 1919, **41**, 1581—1587).—The general plan of a very comprehensive study of the chemotherapeutic value of arsenic compounds is developed. The authors consider that the salvarsan type of these substances has been fully investigated, and therefore turn their attention to products containing quinquevalent arsenic, using as starting point *p*-amino- or *p*-hydroxy-phenylarsinic acid or a similar derivative, and uniting this with an accessible group of simple type which is readily capable of chemical modification. They regard simplicity in chemical manipulation as a further essential to success. From these points of view, the following classes of compounds have been studied: diazoamino-compounds, A–NN–NRR′ (in which A is the arylarsinic radicle and R and R′ hydrogen, alkyl, aryl, or substituted aryl groups),

azo-dyes, A–N:N–R (in which R is the aromatic coupler), *N*-substituted amides of *N*-phenylglycine-*p*-arsinic acid,

$$A–NH·CH_2·CO·NRR'$$

(in which R and R′ are hydrogen, alkyl, aryl, or substituted aryl groups), *β*-substituted carbamides of *N*-phenylglycine-*p*-arsinic acid, $A·NH·CH_2·CO·NH·CO·NHR$, substituted *N*-phenylglycyl derivatives of arsanilic acid, $A–NH·CO·CH_2·NHR$, substituted *o*-phenylglycine derivatives of arsanilic acid, $A–NH·CO·CH_2·OR$, and substituted amides of *o*-phenylglycollic acid and *p*-arsinic acid, $A–o-CH_2·CO·NHR$. Of these, the third type has up to the present yielded the most important results. H. W.

Aromatic Arsenic Compounds. II. The Amides and Alkyl Amides of *N*-Arylglycinearsinic Acids. Walter A. Jacobs and Michael Heidelberger (*J. Amer. Chem. Soc.*, 1919, **41**, 1587—1600. Compare preceding abstract).—The condensation of sodium arsanilate with chloroacetic acid to yield phenylglycine-*p*-arsinic acid has been described previously (D.R.-P. 204664); the authors now find that reaction occurs readily between sodium *p*-aminophenylarsinate and the amide and alkyl amides of chloroacetic acid, yielding substances of the general formula

$$AsO_3H_2·C_6H_3·NH·CH_2·CO·NRR',$$

in which R and R′ may be hydrogen, alkyl, benzyl, or substituted benzyl radicles. The best experimental conditions consist in boiling aqueous solutions of sodium arsanilate and the simpler chloroacetyl alkylamines for a half to two hours; in the case of the chloroacetylbenzylamines, 50% alcohol is the most serviceable medium, and the addition of sodium iodide is found to be necessary.

All the glycineamidearsinic acids are colourless, crystalline substances which are generally sparingly soluble in the usual neutral media and possess high melting or decomposition points, the latter depending greatly on the rate of heating. They dissolve in alkali hydroxides or carbonates to form neutral salts, from which they are entirely displaced by acetic acid. They are more feebly basic than arsanilic acid itself, their hydrochlorides being stable only in the presence of concentrated hydrochloric acid. On boiling with excess of alkali or with mineral acids, the amide linking is hydrolysed, with the formation of glycinearsinic acid and the amine.

The following individual substances are described: N(*phenyl*-p-*arsinic acid*)-*glycineamide* (N-*phenylglycineamide*-p-*arsinic acid*), aggregates of long, thin plates, which darken and soften without melting at 280° when rapidly heated (the *sodium* salt $[+\frac{1}{2}H_2O]$ forms thin, nacreous plates readily soluble in water; the *potassium* and *ammonium* salts crystallise in thin, glistening, hexagonal, microscopic platelets; the *calcium* salt, microscopic, wedge-shaped prisms, is anhydrous; the *magnesium* salt forms a microcrystalline powder; heavy metal salts give immediate precipitates, the *silver* salt forming aggregates of thin, microscopic needles); N(*phenyl*-p-*arsinic acid*)-*glycine methyl ester*, $AsO_3H_2·C_6H_3·NH·CH_2·CO_2Me$.

microscopic needles and thin plates, which soften and darken above 200° and decompose at about 285°; the corresponding *ethyl* ester, delicate needles, m. p. 270° (decomp.); N(*phenyl*-p-*arsinic acid*)-*nitrosoglycineamide*, $AsO_3H_2{\cdot}C_6H_4{\cdot}N(NO){\cdot}CH_2{\cdot}CO{\cdot}NH_2$, silky needles, decomposing at 182–183°; N(*phenyl*-p-*arsinic acid*)-*glycinemethylamide*, microscopic plates, which darken and soften above 240° and decompose at 285°; N(*phenyl*-p-*arsinic acid*)-*glycine-ethylamide*, platelets, decomposing at 278–280° after darkening above 250°; N(*phenyl*-p-*arsinic acid*)-*glycine*-n-*propylamide*, microscopic needles, which do not melt below 280°; N(*phenyl*-p-*arsinic acid*)-*glycinedimethylamide*, microscopic needles, decomposing at about 241–242° when rapidly heated (the *sodium* salt, $+4H_2O$, is described); N(*phenyl*-p-*arsinic acid*)-*glycinediethylamide*, short needles, m. p. 199–201° (decomp.) after softening and darkening above 195°; N(*phenyl*-p-*arsinic acid*)-*glycine-piperidide*, microscopic needles, decomposing at 218–221° after softening and darkening above 200°; N(*phenyl*-p-*arsinic acid*)-*glycinebenzylamide*, microscopic needles, decomposing at 282–284°; N(*phenyl*-p-*arsinic acid*)-*glycine-3'-carboxylamidobenzylamide*, $AsO_3H_2{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$, aggregates of microscopic needles, decomposing at 237–239° with preliminary darkening (the *sodium* salt, $+5H_2O$, is described); N(*phenyl*-p-*arsinic acid*)-*glycine-4'-acetylaminobenzylamide*, diamond-shaped plates, which do not melt below 280° (the *sodium* salt forms microscopic needles, $+4{\cdot}5H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycine-3'-carboxylcarbamidobenzylamide*, $AsO_3H_2{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$, delicate needles, decomposing at 239–240°; N(*phenyl*-p-*arsinic acid*)-*glycine-4'-carbamidobenzylamide*, $AsO_3H_2{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NH_2$; N(*phenyl*-p-*arsinic acid*)-*glycine-3'-methyl-4'-acetylaminobenzylamide*, flat needles, decomposing at 278° (the *sodium* salt, $+6H_2O$, is described); N(*phenyl*-p-*arsinic acid*)-α-*aminopropionamide*, thin, hexagonal plates, darkening above 255° and decomposing at 262–263·5° (the *sodium* salt is described); *oxanilamide*-p-*arsinic acid*, $AsO_3H_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH_2$, minute needles, which do not melt or decompose below 280°.

N(*Phenyl*-o-*arsinic acid*)-*glycineamide* crystallises in thin plates which decompose at 198–199°. N(*Phenyl*-m-*arsinic acid*)-*glycineamide* forms prismatic needles, m. p. 175–177° (decomp.), whilst the corresponding methylamide crystallises in flat, microscopic needles or platelets, m. p. 193–194·5° (decomp.).

The following derivatives of the aminotolylarsinic acids have been prepared: N(*o-tolyl*-4-*arsinic acid*)-*glycineamide*, delicate needles, which do not melt below 285°; N(*o-tolyl*-5-*arsinic acid*)-*glycineamide*, glistening platelets, decomposing at about 283° after darkening above 250°; N(*m-tolyl*-6-*arsinic acid*)-*glycineamide*, diamond-shaped platelets, m. p. 203–207° (decomp.); N-m-2-*tolyl*-5-*arsinic acid glycineamide*, plates or prisms, m. p. 236–237° (decomp.).

H. W.

Aromatic Arsenic Compounds. III. The Carbamides and β-Substituted Carbamides of *N*-Arylglycinearsinic Acids. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, **41**, 1600—1610. Compare preceding abstracts).—By replacing the amides of chloroacetic acid by carbamide and its alkyl or aryl derivatives in the reaction described in the previous paper, the carbamides and substituted carbamides of the arylglycinearsinic acids,

$$AsO_3H_2\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CO\cdot NHR$$

(where R may be hydrogen or an alkyl or aryl radicle), are obtained. The new series of substances closely resembles the amide series; they form stable and soluble neutral salts with the alkali metals. The carbamide linking, like that of the amides, is easily ruptured, this often occurring even at the ordinary temperature in solutions containing excess of alkali hydroxide. From the physiological point of view, the methylcarbamide of *N*-phenylglycine-*p*-arsinic acid is the most interesting member of the series. The following individual substances are described: *Derivatives of* p-*Arsanilic Acid.*—N(*Phenyl*-p-*arsinic acid*)-*glycinecarbamide*, microscopic needles, which darken, but do not melt, below 280° (the *sodium* salt [$+2H_2O$], hexagonal platelets, the *silver* salt, microscopic needles, and the *magnesium* salt are described); N(*phenyl*-p-*arsinic acid*)-*glycinemethylcarbamide*, long, thin, glistening needles, decomposing at 224—225° (the *sodium*, *silver*, and *magnesium* salts were prepared); N(*phenyl*-p-*arsinic acid*)-*glycine-ethylcarbamide*, microscopic needles, decomposing at 223—225° (the *sodium* salt crystallises with $4{\cdot}5H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycinebenzylcarbamide*, rosettes of needles, decomposing at 225°; α-N(*phenyl*-p-*arsinic acid*)-*aminopropionylcarbamide*, $AsO_3H_2\cdot C_6H_4\cdot NH\cdot CHMe\cdot CO\cdot NH\cdot CO\cdot NH_2$, minute needles, which decompose at 225—226°; N(*phenyl*-p-*arsinic acid*)-*glycine-phenylcarbamide*, long, fine needles, which darken and melt at 280° (the *sodium* salt, flat needles [$+5H_2O$], is described); N(*phenyl*-p-*arsinic acid*)-*glycine*-p′-*acetylaminophenylcarbamide*, flat, microscopic needles, decomposing at 265—266° after sintering and darkening above 240° (the *sodium* salt, flat needles [$+5H_2O$], was prepared); N(*phenyl*-p-*arsinic acid*)-*glycine*-m′-*oxamylaminophenylcarbamide*,

$AsO_3H_2\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CO\cdot NH\cdot C_6H_4\cdot NH\cdot CO\cdot CO\cdot NH_2$, microcrystalline powder, decomposing at 223—224°; N(*phenyl*-p-*arsinic acid*)-*glycine*-p′-*hydroxyphenylcarbamide*, microscopic needles ($+1{\cdot}5H_2O$), not melting in the anhydrous state below 280° (the *sodium* salt is described); N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*carbamidophenoxyacetamide*,

$AsO_3H_2\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CO\cdot NH\cdot C_6H_4\cdot O\cdot CH_2\cdot CO\cdot NH_2$, diamond-shaped platelets, decomposing at 243—244° after sintering and darkening (the *sodium* salt forms anhydrous plates); N(*phenyl*-p-*arsinic acid*)-*glycyl*-m′-*carbamidobenzamide*, flat, microscopic needles, m. p. 213—214° (decomp.); N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*carbamidobenzamide*, decomposing at 245° after

darkening above 230°; N(*phenyl*-p-*arsinic acid*)-*glycyl*-m'-*carbamidophenylacetamide*, felted needles, which decompose at 214—216°; N(*phenyl*-p-*arsinic acid*)-*glycyl*-p'-*carbamidophenylacetamide*, needles ($+H_2O$), decomposing when anhydrous at 218—221° (the *sodium* salt forms microscopic, hexagonal platelets).

Derivatives of o-*Arsanilic Acid.*—N(*Phenyl*-o-*arsinic acid*)-*glycinecarbamide*, delicate needles, m. p. 231—232° (decomp.) when rapidly heated; N(*phenyl*-o-*arsinic acid*)-*glycinemethylcarbamide*, minute needles, m. p. 218° (decomp.).

Derivatives of m-*Arsanilic Acid.*—N(*Phenyl*-m-*arsinic acid*)-*glycinecarbamide*, colourless, microscopic needles, decomposing at 208—209°; N(*phenyl*-m-*arsinic acid*)-*glycinemethylcarbamide*, m. p. 213—213·5° (decomp.).

Derivatives of Substituted Arsanilic Acids.—N(m-*Tolyl*-6-*arsinic acid*)-*glycinecarbamide*, delicate needles, decomposing at about 235° (the *sodium* salt forms glistening plates $+2H_2O$); N(m-*tolyl*-6-*arsinic acid*)-*glycinemethylcarbamide*, hair-like needles, decomposing at 218—219°; N(2-*hydroxyphenyl*-5-*arsinic acid*)-*glycinecarbamide*, flat, glistening needles ($+1—1·5H_2O$), decomposing when anhydrous at 203—205°. H. W.

Aromatic Arsenic Compounds. IV. Aromatic Amides of *N*-Arylglycinearsinic Acids. Walter A. Jacobs and Michael Heidelberger (*J. Amer. Chem. Soc.*, 1919, **41**, 1610—1644. Compare preceding abstracts).—An extensive series of compounds has been prepared in accordance with the general scheme:

$$AsO_3HNa\cdot C_6H_4\cdot NH_2 + Cl\cdot CH_2\cdot CO\cdot NHAr \longrightarrow AsO_3H_2\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NHAr + NaCl.$$

In the cases of the more reactive chloroacetyl derivatives, reaction may be effected in boiling aqueous solution, but with the more stable compounds, 50% alcohol is a more suitable solvent, and sodium iodide should be added. In general, it is found that m-arsanilic acid condenses more readily than the ortho- or para-isomerides. The compounds have generally weakly basic and acidic functions; the free arsinic acids do not, as a rule, possess sharp melting or decomposition points, the values obtained depending greatly on the rate of heating. They are, on the whole, but sparingly soluble in the usual media. The sodium salts, on the other hand, dissolve more or less readily in water, and were prepared for convenience in biological testing, and also as a convenient means of purification of the compounds. The following individual substances are described.

Derivatives of p-*Arsanilic Acid.*—N(*Phenyl*-p-*arsinic acid*)-*glycineanilide*, $AsO_3H_2\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NHPh$, minute, delicate needles, which do not melt below 285° (the *sodium* salt, glistening scales $[+4H_2O]$, and the *nitroso*-compound, flat, colourless needles $[+H_2O]$, decomposing at 190—192°, are described); N(*phenyl*-p-*arsinic acid*)-*glycine*-o'-*toluidide*, needles, which are not decomposed

below 275° (*sodium* salt, long, narrow platelets [$+2{\cdot}5H_2O$]); N(*phenyl*-p-*arsinic acid*)-*glycine*-m′-*toluidide*, long, thin plates decomposing at 285°; N(*phenyl*-p-*arsinic acid*)-*glycine*-p′-*toluidide*, woolly masses of minute needles, which do not decompose below 280° (*sodium* salt, thin, curved, glistening needles $+3H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycine*-α-*naphthylamide*, microscopic needles, which darken, but do not melt, below 280°; N(*phenyl*-p-*arsinic acid*)-*glycine*-β-*naphthylamide*, microscopic needles, decomposing at 285—286° to a red liquid (*sodium* salt, flat needles $+4{\cdot}5H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycinediphenylamide*, long, thin, microscopic leaflets ($+H_2O$), decomposing when anhydrous at 271—272°; N(*phenyl*-p-*arsinic acid*)-*glycine*-p′-*chloroanilide*, toothed, microscopic leaflets, which do not melt below 280°; N(*phenyl*-p-*arsinic acid*)-*glycine*-p′-*iodoanilide*, broad, minute needles, which do not melt below 275° (*sodium* salt, needles $+3{\cdot}5H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycine*-p′-*nitroanilide*, thin, faintly yellow needles, not melting below 285°; N(*phenyl*-p-*arsinic acid*)-*glycine*-p′-*acetylaminoanilide*, microscopic needles, which do not melt below 285° (*sodium* salt, minute, lustrous platelets); N(*phenyl*-p-*arsinic acid*)-*glycine*-p′-*aminoanilide* (by hydrolysis of the acetyl derivative or reduction of the corresponding nitro-compound), colourless, microscopic needles or platelets, decomposing at 253—254°; N(*phenyl*-p-*arsinic acid*)-*glycine*-p′-*carbamidoanilide*, pale brown, microcrystalline aggregates ($+0{\cdot}5H_2O$), decomposing when anhydrous at 230° after darkening above 200° (*sodium* salt, microscopic needles $+4H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycine*-4′-*methyl*-5′-*carbamidoanilide*, microscopic platelets and hairs, decomposing at 257—258° (*sodium* salt, crystalline powder $+3{\cdot}5H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycine*-m′-*aramylaminoanilide*,

$AsO_3H_2{\cdot}C_6H_3{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH_2$,

microcrystalline aggregates, which darken and partly decompose, but do not melt below 280°; N(*phenyl*-p-*arsinic acid*)-*glycyl*-o′-*aminophenol*, lustrous crystals, m. p. 190° (decomp.) after preliminary darkening; N(*phenyl*-p-*arsinic acid*)-*glycine*-m′-*hydroxyanilide*, which is of special importance, owing to its reduction to arsenophenylglycinebis-*m*′-hydroxyvanilide; N(*phenyl*-p-*arsinic acid*)-*glycine*-4-*hydroxy*-o-*toluidide*, pink plates or prisms, decomposing at about 220—225°; N(*phenyl*-p-*arsinic acid*)-*glycine*-2′-*hydroxy*-p-*toluidide*, prisms, m. p. 258° (decomp.); N(*phenyl*-p-*arsinic acid*)-*glycine*-p′-*hydroxyanilide*, glistening platelets, m. p. 255—260° (decomp.) (*sodium* salt, lustrous leaflets $+4{\cdot}5H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycine*-p′-*anisilide*, lustrous leaflets, which darken and soften above 230°; N(*phenyl*-p-*arsinic acid*)-*glycine*-1-*hydroxy*-β-*naphthalide*, microscopic plates and prisms ($+2H_2O$), decomposing, when anhydrous, at 189—191°; N(*phenyl*-p-*arsinic acid*)-*glycine*-4-*hydroxy*-α-*naphthalide*, microscopic crystals, decomposing, when anhydrous, at 240—242° after darkening above 200° (*sodium* salt, glistening plates $+5{\cdot}5H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycyl*-4:6-*dichloro*-3-*hydroxyanilide*, flat, colourless, microscopic needles, m. p. about 280° (decomp.) after darkening above 200°; N(*phenyl*-p-*arsinic*

acid)-*glycyl*-6-*bromo*-3-*hydroxyanilide*, glistening leaflets, decomposing at 255°; N(*phenyl*-p-*arsinic acid*)-*glycine*-3′:4′-*dihydroxyanilide*, glistening leaflets, decomposing at about 260—265° after blackening above 200°; N(*phenyl*-p-*arsinic acid*)-*glycylanthranilic acid*, octahedra, which decompose at 230—235° (the corresponding *ethyl* ester forms needles which do not decompose below 280°); N(*phenyl*-p-*arsinic acid*)-*glycyl*-N-*methylanthranilic acid*, microscopic aggregates of needles or plates, decomposing at 230°; N(*phenyl*-p-*arsinic acid*)-*glycyl*-2′-*aminobenzamide*, microscopic needles ($+H_2O$), m. p. 170° (*sodium* salt, minute crystals $+4{\cdot}5H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycyl*-m′-*aminobenzamide*, irregular, microscopic platelets, which are not completely decomposed below 280°; N(*phenyl*-p-*arsinic acid*)-*glycyl*-m′-*aminobenzoylcarbamide*, microscopic needles, decomposing at about 280° (*sodium* salt, microscopic hairs $+8H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*aminobenzamide*, microscopic needles, which do not melt below 280° (*sodium* salt, thin, microscopic needles $+4{\cdot}5H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycyl*-5′-*aminosalicylamide*, glistening scales ($+H_2O$), which, when anhydrous, softens above 190° and gradually decomposes until fluid at about 255°; N(*phenyl*-p-*arsinic acid*)-*glycyl*-m′-*aminophenylacetamide*, microscopic needles, decomposing at 275—280° after darkening above 220°; N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*aminophenylacetic acid*, microscopic globules, m. p. 280° (decomp.); N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*aminophenylacetamide*, microscopic hairs, which do not decompose below 280° (*sodium* salt, glistening platelets $+4{\cdot}5H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*aminophenylacetylcarbamide*, minute hairs, which do not melt below 280° (*sodium* salt, minute, hexagonal plates $+3H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycyl*-o′-*aminophenoxyacetamide*, minute needles, decomposing at about 280° with preliminary darkening; N(*phenyl*-p-*arsinic acid*)-*glycyl*-m′-*aminophenoxyacetic acid*, decomposing at about 250—260° after softening at 180—190°; N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*aminophenoxyacetic acid*, flat, microscopic needles or platelets, which do not melt below 285° (*sodium* salt, glistening leaflets $+3H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*aminophenoxyacetamide*, flat needles, which do not melt below 280° (*sodium* salt, microscopic needles $+5H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*aminophenoxyacetylcarbamide*, microscopic needles, slowly decomposing at 290° (*sodium* salt, microscopic needles $+4H_2O$); N(*phenyl*-p-*arsinic acid*)-*glycyl*-3-*methyl*-4-*aminophenoxyacetic acid*, microscopic needles, decomposing at 270° (*sodium* salt, well-defined needles); N(*phenyl*-p-*arsinic acid*)-*glycyl*-m′-*aminobenzenesulphonamide*, flat, glistening needles, which decompose at about 265° with preliminary darkening; N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*aminobenzenesulphonic acid*, flat needles ($+2H_2O$), slowly decomposing when anhydrous, at 245—246°; N(*phenyl*-p-*arsinic acid*)-*glycyl*-p′-*aminobenzenesulphonamide*, thin, microscopic leaflets and needles, which do not melt below 280°; N(*phenyl*-p-*arsinic acid*)-*glycyl*-4-*amino*-6-*hydroxybenzenesulphonic acid*, microscopic leaflets ($+1{\cdot}5H_2O$), which, when anhydrous, softens and darkens above

200°, but does not melt below 275°; N(*phenyl*-p-*arsinic acid*)-*glycyl*-4-*aminoacetophenone*, long, fine hairs, which do not melt below 280°.

Derivatives of o-*Arsanilic Acid.*—N(*Phenyl*-o-*arsinic acid*)-*glycineanilide*, minute prisms ($+1H_2O$), melting with decomposition at 160—163° when anhydrous; N(*phenyl*-o-*arsinic acid*)-*glycine*-o′-*hydroxyanilide*, glistening needles ($+0{\cdot}5H_2O$), m. p. (anhydrous) 151—153° (decomp.); N(*phenyl*-o-*arsinic acid*)-*glycine*-m′-*hydroxyanilide*, pink, microscopic platelets ($+2H_2O$), m. p. 103—105°, m. p. of anhydrous substance about 180° (decomp.) after softening at about 125—130°; N(*phenyl*-o-*arsinic acid*)-*glycine*-p′-*hydroxyanilide*, colourless, microscopic platelets, m. p. 208—209° (decomp.).

Derivatives of m-*Arsanilic Acid.*—N(*Phenyl*-m-*arsinic acid*)-*glycineanilide*, prisms, decomposing at 217—218°; N(*phenyl*-m-*arsinic acid*)-*glycine*-o′-*hydroxyanilide*, flat, microscopic needles, m. p. 190—192° (decomp.) (the *ammonium* salt forms minute needles); N(*phenyl*-m-*arsinic acid*)-*glycine*-m′-*hydroxyanilide*, minute, irregular platelets and flat needles ($+1{\cdot}5H_2O$), decomposing, when anhydrous, at about 180—190°; N(*phenyl*-m-*arsinic acid*)-*glycine*-p′-*hydroxyanilide*, microscopic platelets, which slowly decompose at 180°.

Derivatives of Substituted and p-*Arsanilic Acids.*—N(o-*Tolyl*-5-*arsinic acid*)-*glycine*-m′-*hydroxyanilide*, long, flat, microscopic needles, which slowly darken and decompose at 235°; N(o-*tolyl*-5-*arsinic acid*)-*glycine*-p′-*hydroxyanilide*, spindle-shaped needles, decomposing at 232—233° with preliminary darkening; N(m-*tolyl*-6-*arsinic acid*)-*glycine*-m′-*hydroxyanilide*, spindle-shaped microcrystals, which decompose at 232—235° after softening and darkening; N(2-*carboxyphenyl*-4-*arsinic acid*)-*glycine*-m′-*hydroxyanilide*, minute platelets ($+1H_2O$), decomposing, when anhydrous, at 204—207° after darkening and swelling. H. W.

Aromatic Arsenic Compounds. V. *N*-Substituted Glycylarsanilic Acids. Walter A. Jacobs and Michael Heidelberger (*J. Amer. Chem. Soc.*, 1919, **41**, 1809—1821. Compare preceding abstracts).—The substances under discussion are closely related to the previously described substituted anilides of phenylglycine-*p*-arsinic acid, but differ from these in the fact that the glycine side-chain is reversed, the arsinic radicle becoming a substituent on the anilide nucleus. The substances are readily prepared by boiling the sodium salt of chloroacetylarsanilic acid with the aromatic amino-compound in aqueous solution. The substituted phenylglycylarsanilic acids closely resemble the isomeric anilides of phenylglycine-*p*-arsinic acid, functioning both as acids and feeble bases. They are but sparingly soluble in the usual media, and all have high melting or decomposition points, the observed values depending on the rate of heating. In general, the sodium salts are readily soluble in water. The following individual substances have been prepared.

Chloroacetyl-*p*-arsanilic acid, $AsO_3H_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2Cl$ (compare D.R.-P. 191548), conveniently prepared by heating dry chloroacetic acid with *p*-arsanilic acid on the water-bath, minute, lenticular platelets and toothed leaflets, m. p. 285° (decomp.); *glycyl*-p-*arsanilic acid*, glistening plates, which do not melt below 295° (*iminobisacetyl*-p-*arsanilic acid*, micro-crystals, darkening without melting at 280—285°, is formed as by-product of the action of aqueous ammonia on chloroacetyl-*p*-arsanilic acid); N-*methylglycyl*-p-*arsanilic acid*, silky, glistening needles ($+2H_2O$), which darken at about 250°, but do not melt below 275°; N-*phenylglycyl*-p-*arsanilic acid*, felted needles, which do not melt below 280°; m-*oxaminophenylglycyl*-p-*arsanilic acid*,

$CO_2H{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}AsO_3H_2$,

decomposing, when anhydrous, at 179°, hydrated acid $+1H_2O$ (the *hydrochloride* is described); p-*aminophenylglycyl*-p-*arsanilic acid*, microcrystalline aggregates, which darken and soften, but do not melt, below 280°; p-*acetylaminophenylglycyl*-p-*arsanilic acid*, hexagonal platelets, not melting below 275° (the *sodium* salt forms flat, glistening needles $+7H_2O$); p-*oxaminophenylglycyl*-p-*arsanilic acid*, microscopic crystals $+1{\cdot}5H_2O$, darkening in the anhydrous state above 200°, but not melting below 275°; *p-oxamylaminophenylglycyl*-p-*arsanilic acid*, microscopic needles, not melting below 285° (the *sodium* salt was prepared); p-*carbamidophenylglycyl*-p-*arsanilic acid*, microscopic leaflets, which do not melt below 285°; m-*hydroxyphenylglycyl*-p-*arsanilic acid*, prisms $+3{\cdot}5H_2O$, which melt in their water of crystallisation at about 80° (the *hydrochloride* is described); p-*hydroxyphenylglycyl*-p-*arsanilic acid*, microscopic hairs ($+1H_2O$), which, when anhydrous, blacken and sinter above 200°, but do not melt entirely below 280° (the *sodium* salt, aggregates of microscopic needles $+H_2O$, was prepared); m-*carboxylamidophenylglycyl*-p-*arsanilic acid*, microscopic needles, decomposing at 248° (*sodium* salt, radiating masses of flat needles $+1H_2O$); *N-phenylglycineanilide*-m-*carboxycarbamide*-p'-*arsinic acid*,

$AsO_3H_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$,

microscopic needles, decomposing at about 280° (*sodium* salt, flat, microscopic needles $+3H_2O$); p-*carboxylamidophenylglycyl*-p-*arsanilic acid*, microscopic prisms, which do not melt below 275° (*sodium* salt, glistening platelets $+2H_2O$); *N-phenylglycineanilide*-p-*acetamide*-p'-*arsinic acid*,

$AsO_3H_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO{\cdot}NH_2$,

microscopic platelets, decomposing at 256—258° after darkening and softening above 180°; N-*phenylglycineanilide*-p-*acetylcarbamide*-p'-*arsinic acid*, microscopic hairs $+0{\cdot}5H_2O$, which decompose, when anhydrous, at 270—273° after darkening above 230°; *N-phenylglycineanilide*-p-*oxyacetic*-p'-*arsinic acid*,

$AsO_3H_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CO_2H$,

minute, wedge-shaped plates $+1{\cdot}5H_2O$, decomposing in the anhydrous state at about 275° after darkening above 180°; *N-phenylglycineanilide*-p-*oxyacetamide*-p'-*arsinic acid*, woolly needles not melting below 265° (*sodium* salt, rosettes of flat, glistening needles $+4H_2O$); N-*phenylglycineanilide*-p-*oxyacetocarb-*

amide-p'-*arsinic acid*, minute platelets, which decompose at 257 258° with preliminary darkening (*sodium* salt, minute leaflets $+4H_2O$); N-*phenylglycineanilide*-p-*glycineamide*-p'-*arsinic acid*, micro-crystals ($+1{\cdot}5H_2O$), which, when anhydrous, do not melt below 285°; N-*phenylglycineanilide*-4:4'-*diarsinic acid*,

$$AsO_3H_2{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}AsO_3H_2,$$

microscopic needles ($+0{\cdot}5H_2O$), not melting below 280° when anhydrous; p-*acetylphenylglycyl*-p-*arsanilic acid*, microscopic needles, which darken and decompose when heated, but do not melt below 290° (*sodium* salt, pale yellow, glistening platelets $+3H_2O$).

H. W.

Aromatic Arsenic Compounds. VI. *N*-(Phenyl-*p*-arsinic acid)-α-phenylglycine and its Amides. Walter A. Jacobs and Michael Heidelberger (*J. Amer. Chem. Soc.*, 1919. **41**, 1822—1825. Compare preceding abstracts).—As a special extension of the general type of substances represented by the substituted amides, carbamides, and anilides of the phenylglycinearsinic acids, *N*(phenyl-*p*-arsinic acid)-α-phenylglycine,

$$AsO_3H_2{\cdot}C_6H_4{\cdot}NH{\cdot}CHPh{\cdot}CO_2H,$$

its amide, carbamide, and certain substituted anilides have been prepared. With the exception of the glycine itself, which was obtained by hydrolysis of the amide, the substances were made from sodium arsanilate and the phenylchloroacetylamino-compounds. It was found necessary to use sodium iodide and 50% alcoholic solution. The general properties of this group of substances are similar to those of the simpler glycine derivatives.

The following compounds are described: *N*(*phenyl*-p-*arsinic acid*)-α-*phenylglycine*, lustrous, rhombic plates, decomposing at 202—203° after darkening and softening; *N*(*phenyl*-p-*arsinic acid*)-α-*phenylglycineamide*, microscopic needles, which do not melt below 280° (*sodium* salt, granular aggregates of plates $+3{\cdot}5$ to $5H_2O$); *N*(*phenyl*-p-*arsinic acid*)-α-*phenylglycinecarbamide*, microscopic needles $+1H_2O$, decomposing when anhydrous at 195—197°; *N*(*phenyl*-p-*arsinic acid*)-α-*phenylglycine*-3'-*hydroxyanilide*, lenticular platelets $+1{\cdot}5H_2O$, decomposing at 155—160°; the anhydrous substance has m. p. about 200—210° (decomp.), after softening at about 155—160°; *N*(*phenyl*-p-*arsinic acid*)-α-*phenylglycine*-4'-*carbamidoanilide*, decomposing at about 255° with preliminary darkening and softening; *N*(*phenyl*-p-*arsinic acid*)-α-*phenylglycine*-3'-*carbamidoanilide*, microcrystalline powder, m. p. 261—262° (decomp.); *N*(*phenyl*-p-*arsinic acid*)-α-*phenylglucyl*-4-*aminophenylacetamide*, $AsO_3H_2{\cdot}C_6H_3{\cdot}NH{\cdot}CHPh{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, minute plates and flat needles $+0{\cdot}5H_2O$, melting in the anhydrous condition at 222—223° (decomp.).

H. W.

Aromatic Arsenic Compounds. VII. Substituted Benzyl-, Phenoxyethyl- and Phenacyl-arsanilic Acids. Walter A. Jacobs and Michael Heidelberger (*J. Amer. Chem. Soc.*, 1919. **41**, 1826—1833. Compare preceding abstracts).—It has been

hown previously that the reactivity of the amino-group in arsanilic cid with chloroacetylamino-compounds is such as to render possible he synthesis of a very extensive series of aromatic arsinic acids. 'he authors now describe a preliminary series of experiments with ther aromatic derivatives containing suitable alkyl haloid side-hains. Thus benzyl and substituted benzyl chlorides react with odium arsanilate under suitable conditions to form benzyl- and ubstituted benzyl-arsanilic acids, reaction proceeding readily with egatively substituted benzyl chlorides. Similarly, the required erivatives are slowly formed from phenoxyethyl bromide and allied ubstances, whilst with phenacyl haloids the reaction also proceeds in the desired sense.

The following individuals are described: *benzyl*-p-*arsanilic acid*, arborescent masses of micro-crystals and larger prisms, decomposing at about 255° (*sodium* salt, glistening platelets); p-*nitrobenzyl-arsanilic acid*, yellow, microscopic needles, which do not melt below 280°; p-*aminobenzylarsanilic acid* (by reduction of the *p*-nitro-acid with ferrous hydroxide), microscopic leaflets, decomposing at about 202°; 3-*nitro*-4-*hydroxybenzylarsanilic acid*, minute, yellow crystals ($+1H_2O$), decomposing when anhydrous at about 245—250° after darkening and sintering above 210° (*sodium* salt, thin, yellow, microscopic needles); 3-*amino*-4-*hydroxybenzylarsanilic acid*, microscopic platelets ($+0{\cdot}5H_2O$), which do not melt below 285° when anhydrous; p-*carboxybenzylarsanilic acid*, microscopic needles which do not melt below 280° (*sodium* salt, microcrystalline powder $+0{\cdot}5H_2O$); p-*carboxylamidobenzylarsanilic acid*, microscopic needles, not melting below 280° (*sodium* salt, thin plates $+2{\cdot}5H_2O$).

Phenoxyethylarsanilic acid, $OPh{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}AsO_3H_2$, glistening scales ($+1H_2O$), which, when anhydrous, do not melt below 280° (*sodium* salt, flat, microscopic needles $+3{\cdot}5H_2O$); p-*acetylaminophenoxyethylarsanilic acid*, thin, narrow plates which do not melt below 275° (*sodium* salt, colourless, microscopic platelets $+3H_2O$); o-*carboxylamidophenoxyethylarsanilic acid*, broad, microscopic needles not melting below 280°; *phenacylarsanilic acid*, $COPh{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}AsO_3H_2$, faintly yellow aggregates of delicate, microscopic needles, which decompose at 185—187°; 2-*hydroxy*-5-*acetylaminophenacylarsanilic acid*, microscopic platelets, decomposing at 228°. [3-*Acetylamino*-6-*hydroxyphenacyl bromide*, from acetophenetidide, bromoacetyl chloride and aluminium chloride, forms a drab-coloured powder, m. p. 133—135° (slight decomp.).] H. W.

Aromatic Arsenic Compounds. VIII. The Amides of (p-Arsinic Acid)-phenoxyacetic Acid and the Isomeric Phenoxyacetylarsanilic Acids. Walter A. Jacobs and Michael Heidelberger (*J. Amer. Chem. Soc.*, 1919, **41**, 1834—1840. Compare preceding abstracts).—Chloroacetylamino-compounds react with sodium *p*-hydroxyphenylarsinate (compare D.R.-P. 216270) to yield arsinic acids which crystallise readily when pure, have high decomposition points, are sparingly soluble in the usual media, and are more strongly acidic than the amides of phenylglycinearsinic acid. The success of the condensation depends on the addition of

an extra molecule of sodium hydroxide in order to form the sodium phenoxide, and this condition depresses the yield in the cases in which the haloid contains a labile halogen atom. Similarly, the sodium salt of chloroacetylarsanilic acid reacts with phenols to yield phenoxyacetyl or phenyl ether glycollylarsanilic acids, which are more strongly acidic than the glycylarsanilic acids. On reduction, both of these groups of substances yield arsenoxides and arseno-compounds which will be more fully described in a later communication.

The following substances have been prepared: *methyl* (p-*arsinic acid*)-*phenoxyacetate*, $AsO_3H_2{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CO_2Me$, lustrous plates, which partly melt at about 192—195° (decomp.); (p-*arsinic acid*)-*phenoxyacetamide*, rhombic, microscopic prisms, which do not melt below 280° (*sodium* salt, glistening platelets); (p-*arsinic acid*)-*phenoxyacetanilide*, minute prisms and microscopic plates, which darken slightly above 250°, but do not melt below 280°; (p-*arsinic acid*)-*phenoxyaceto*-m-*hydroxyanilide*, sandy powder, m. p. 238—240° (decomp.) (*sodium* salt, lustrous, microscopic needles and long, thin platelets); (p-*arsinic acid*)-*phenoxyaceto*-p-*hydroxyanilide*, curved, colourless, microscopic crystals, decomposing at 238—240° (the *sodium* salt and (?) nitroso-compound were prepared); (p-*arsinic acid*)-*phenoxyacetyl*-4-*aminophenylcarbamide*, microscopic needles, which darken and soften at about 230—240°, but do not melt entirely up to 265°.

Phenoxyacetylarsanilic acid, $OPh{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}AsO_3H_2$, colourless crystals which darken slightly above 250°, but do not decompose below 280°; p-*oxaminophenoxyacetylarsanilic acid*, cream-coloured crystals, which darken but do not melt below 280° (a hydrated form $+1H_2O$ is also described); p-*carbamidophenoxyacetylarsanilic acid*, microscopic spindles, decomposing at about 280—283° with preliminary darkening (*sodium* salt, minute needles $+3H_2O$); o-*carbarylamidophenoxyacetylarsanilic acid*, delicate needles which do not decompose below 280° (*sodium* salt, prismatic needles $+5{\cdot}5H_2O$); p-*carbarylamidophenoxyacetylarsanilic acid*, long, glistening needles, not melting below 280° (*sodium* salt, long, flat needles, $+7{\cdot}5H_2O$). H. W.

Action of Arsenic Acid on Polyhydric Phenols. Adolf Sonn (*Ber.*, 1919, **52**, [*B*], 1704).—The polyhydric phenols suffer oxidation when heated with arsenic acid in the usual way, but if pyrogallol and dilute arsenic acid solutions are concentrated in a vacuum and left in the cold, a crystalline *pyrogallol arsenate*, $AsO[O{\cdot}C_6H_3(OH)_2]_3$, is deposited. J. C. W.

1 : 3-Benzodiazolearsinic Acids and their Reduction Products. Robert Reginald Baxter and Robert George Fargher (T., 1919, **115**, 1372—1380).

Organic Mercury Compounds Derived from *p*-Bromodimethylaniline. Frank C. Whitmore (*J. Amer. Chem. Soc.*, 1919, **41**, 1841—1854).—The paper is the first of a series in which the introduction of mercury in the ortho-position to various substi-

tuted amino-groups will be studied. The reactions involved may be represented by the single equilibrium equation, $R_2Hg + HgX_2 \rightleftarrows 2RHgX$, in which R represents any organic residue which has its free bond attached to carbon and X represents any univalent acid radicle. The reaction normally runs to completion to the right because of the slight solubility of the organo-mercuric salt, RHgX, in the organic solvents used. It may, however, be reversed by using reagents which remove HgX_2, such as alkaline reducing agents and compounds like potassium iodide and sodium thiosulphate, which form mercuric complexes of considerable stability.

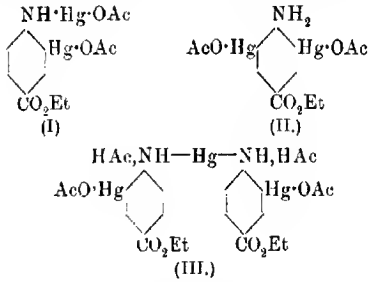
5-*Bromo*-2-*dimethylaminophenylmercuriacetate*, $NMe_2 \cdot C_6H_3Br \cdot HgC_2H_3O_2$, colourless needles, m. p. 144°, is prepared by the action of mercuric acetate on *p*-bromodimethylaniline in cool, aqueous alcoholic solution in 74% yield; simultaneously, smaller quantities of mercurous acetate and of a tar are produced. Formation of the latter is more pronounced in warm, concentrated solution; it can be suppressed to some extent by gradually adding the mercuric acetate to the well-agitated solution, but the yield of the mercury derivative also suffers. The mercury is not precipitated by hydrogen sulphide. The corresponding *chloride*, very fine needles, m. p. 183°, *bromide*, m. p. 182°, *iodide*, m. p. 169°, and *thiocyanate*, white, gritty crystals, m. p. 135°, decomposing at 140°, were obtained by the action of alcoholic solutions of the acetate on alcoholic solutions of calcium chloride, sodium bromide, potassium iodide, and potassium thiocyanate respectively. 5-*Bromo*-2-*dimethylaminophenylmercurihydroxide*, from the acetate and sodium hydroxide in alcoholic solution, forms hard, nodular masses of crystals, m. p. 162°, and evolves gas without blackening at 165°. The *formate*, from the hydroxide and ethyl formate, crystallises in fine, felted needles, m. p. 145°, and decomposes at 150°.

Mercury di-5-*bromo*-2-*dimethylaminophenyl*, colourless needles, m. p. 123°, is most conveniently prepared (86% yield) by boiling a solution of the acetate in alcohol with potassium iodide, but the formation of *p*-bromodimethylaniline could not be suppressed completely. Reaction appears to depend on the formation of a stable iodine complex, M_2HgX_4, and evidence in support of this hypothesis is afforded by experiments with sodium or ammonium bromide or calcium chloride. The complexes formed by bromine and chlorine are less stable than those formed by iodine, and the yield of the mercury diphenyl compound drops to 3% with the bromides and to zero with the chloride. Conversion of the acetate into the mercury diphenyl derivative is less advantageously effected with sodium stannite solution (yield, 63%), and only very unsatisfactorily with sodium thiosulphate or potassium sulphide; with the latter reagent the *sulphide* was isolated as hard, white flakes which become grey at about 97° and partly melted at 115—120°. The formate, when heated for a protracted period in benzene alcoholic solution, yielded mainly mercury and *p*-bromodimethylaniline and a small quantity of the mercury diphenyl compound. Reduction of the acetate by

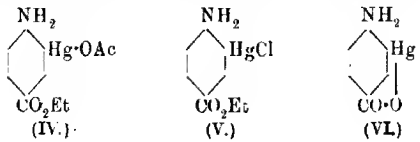
zinc dust in boiling alcoholic solution gave mercury, unchanged acetate, and *p*-bromodimethylaniline; with copper powder under similar conditions very little reaction occurred.

The mercury diphenyl derivative is quantitatively transformed into 5-bromo-2-dimethylaminophenylmercurichloride when heated with mercuric chloride in the presence of alcohol; the bromide, iodide, and thiocyanate may be obtained similarly and in good yield, but the iodide obtained in this manner is not nearly so pure as the corresponding bromide or chloride. When the mercury diphenyl derivative is heated in an analogous manner with mercuric sulphate, it yields basic mercuric sulphate and *p*-bromodimethylaniline. H. W.

The Doctrine of Substitution. II. Mercuration of Ethyl *p*-Aminobenzoate. WALTER SCHOELLER, WALTER SCHRAUTH and ERWIN LIESE (*Ber.*, 1919, **52**, [*B*], 1777—1787. Compare A., 1914, i, 892).—When ethyl *p*-aminobenzoate is left with mercuric acetate in cold methyl alcohol, a pale yellow precipitate of *ethyl* N:3-*diacetoxydimercuri*-4-*aminobenzoate* (I), m. p. 245°, is slowly deposited.



This is converted into *ethyl* 3:5-*diacetoxydimercuri*-4-*aminobenzoate* (II), a felted mass of long needles, m. p. 255—257°, on warming with glacial acetic acid, this being formed directly if acetic acid is used as the solvent in the first condensation. In a mixture of methyl alcohol and acetic acid, however, the white, microcrystalline *substance* (III), m. p. 230—240°, is produced. This is resolved into compound (I) and *ethyl* 3-*acetoxymercuri*-4-*aminobenzoate* (IV) (bundles of white needles, m. p. 182°, and again at 228°) on boiling with methyl alcohol, and into compounds (II) and (IV) on warming with glacial acetic acid. Compound (IV) is best obtained by melting the original agents together, when at 160° the mass solidifies again



and the desired product may be extracted by hot methyl alcohol. Compounds (I) and (IV) react with sodium chloride in a mixture of methyl alcohol and acetic acid to form *ethyl 3-chloromercuri-4-aminobenzoate* (V), which crystallises in small, white prisms, m. p. 223°, but compound (II) differs from compound (I) in forming *ethyl 3:5-dichlorodimercuri-4-aminobenzoate*, small needles, m. p. 270°, under these conditions. When boiled with dilute sodium hydroxide, compound (IV) loses the ester and acetyl groups, and the sodium salt so formed deposits flocculent, white *3-hydroxymercuri-4-aminobenzoic anhydride* (VI) on acidification.

As a proof that the amino-group is free in compound (II), which is a type not produced in the case of anthranilic acid, the formation of its *acetyl* derivative (small needles, m. p. 247°) is advanced.

J. C. W.

Physiological Chemistry.

The Absence of the Bromine Reaction for Tryptophan in Tryptically Digested Leucocytes. Moritz Weiss (*Biochem. Zeitsch.*, 1919, **98**, 116—120).—Tryptically digested leucocytes do not give the bromine reaction for tryptophan. Putrified pus shows the presence of indole, but only traces of indole derivatives can be demonstrated in it by the urorosein reaction (hydrochloric acid and sodium nitrite). The pus cells give a strong Adamkiewicz-Liebermann reaction. Whilst casein manifests a blue coloration, leucocytes give a violet coloration in this reaction. It is concluded that a derivative of tryptophan, but not tryptophan itself, is concerned in the synthesis of leucocytes. S. S. Z.

Origin of Odour. H. Teudt (*Deutsch. Essigind.*, 1919, **23**, 160–162; from *Chem. Zentr.*, 1919, iii, 239).—The author has been able to develop his theory further by a consideration of the atomic models of Rutherford and Bohr, and has deduced the causes which are operative in setting the valency electrons within the molecule into such vibrations as produce odour (compare A., 1919, i, 607). The original paper must be consulted for details. H. W.

The Chromium Reaction of Certain Tissues as an Adrenaline Reaction. W. Stoeltzner (*Münch. med. Woch.*, 1919, **66**, 584; from *Chem. Zentr.*, 1919, iii, 60).—It has not been observed previously that adrenaline gives the same reaction with chromic acid as certain tissues. A dilute, pale yellow solution of potassium dichromate becomes intensely brown after addition of adrenaline, and gradually deposits a brown precipitate. The shade exactly matches the brown coloration assumed by the tissue when treated with dichromate, and the chromium reaction of the tissue must therefore be due to adrenaline. H. W.

Presence of Hæmatoporphyrin in the Urine and Fæces of a Case of Acute Hæmatoporphyrinuria. Wilhelm Löffler (*Biochem. Zeitsch.*, 1919, **98**, 105—116).—The coloured urine of a patient suffering from Landry's disease was examined for hæmatoporphyrin. The urine was precipitated with glacial acetic acid and the precipitate dissolved in potassium hydroxide. After reprecipitating and redissolving in *N*/10-potassium hydroxide, the fraction showed the typical spectrum of hæmatoporphyrin. A portion of the hæmatoporphyrin was methylated by H. Fischer's method. The compound thus obtained melted at 262° (not sharp), and gave the same spectrum as Fischer's preparation. The hydrolysed methyl ester yielded the original hæmatoporphyrin.

0·2 Gram of hæmatoporphyrin was excreted in twenty-four hours. On extracting the fæces of the same patient by Fischer's bicarbonate method and with methyl alcohol and hydrochloric acid the presence of small quantities of hæmatoporphyrin similar to that extracted by Fischer from a similar source was established.

S. S. Z.

The Action of Strophanthin on Colloids. Georg Pietrkowski (*Biochem. Zeitsch.*, 1919, **98**, 92—104).—The action of strophanthin on optically invisible colloidal gold solutions produces an increase in the number of particles visible under the ultra-microscope. In the case of an hydrophile colloid, such as gelatin, strophanthin inhibits imbibition. These facts, it is suggested, justify the conclusion that the increase in tonus in the cardiac muscles brought about by the action of this drug is due to the shrinking of the surface of the muscle fibres. The above experiments, however, do not explain the specificity of strophanthin. S. S. Z.

Chemistry of Vegetable Physiology and Agriculture

Butylene Glycol Fermentation of Sucrose by Bacteria of the Prodigiosus Group. M. Lemoigne (*Compt. rend. soc. biol.*, 1919, **82**, 234—236; from *Chem. Zentr.*, 1919, iii, 198).—In addition to acid and traces of ethyl alcohol and acetaldehyde, $\beta\gamma$-butylene glycol and acetylmethylcarbinol are invariably found among the products of the decomposition of sucrose by different varieties of *B. prodigiosus*. The bacteria, therefore, ferment sucrose in the same manner as those of the group of *B. subtilis*, *B. lactis aerogenes*, and *Staphylococci* (A., 1913, i, 1422). H. W.

The Alkali-forming Bacteria found in Milk. S. Henry Ayers, Philip Rupp, and William T. Johnson, jun. (*U.S. Dept. of Agriculture*, 1919, Bull. No. 782).—The group of bacteria

studied is defined as consisting of those which produce an alkaline reaction in milk without peptonisation of the casein. This group produced the reaction in five days at 30°. The reaction was not due to ammonia, as ammonia was produced by a few organisms only, and then not until the second week. All the citric acid in the milk was used up, and an amount of carbonate corresponding with about half the citric acid was produced. The chief sources of these organisms were milk, soil, and water. Of the species studied, six were cocci and sixty-two were bacilli; all were non sporing, and had an optimum temperature of 20—30°.

The action of each organism on certain organic compounds was examined, using cultivations in a sodium ammonium phosphate medium containing the test substance as the only source of carbon. The change in the hydrogen-ion concentration was taken as the measure of the alkalinity produced. It was found that dextrose and galactose were fermented by forty-four cultures, lactose by eleven, saccharose by two, and raffinose by none. Ethyl, propyl, and amyl alcohols were more readily fermented than mannitol and glycerol. The sodium salts of many organic acids were also used, with the result that pyruvic, citric, malic, lactic, succinic, acetic, propionic, butyric, valeric, hexoic, mucic, glyceric, tartaric, malonic, formic, benzoic, and salicylic acids were converted into carbonates, and oxalic and glycollic acids were unacted on. *n*-Butyric, *n*-valeric, and *n*-hexoic acids were first converted into simpler acids. An investigation of the results showed that the organisms took their carbon most readily from the alkyl and primary alcohol groups, provided the primary alcohol was not linked to a carboxyl group. A secondary alcohol group was less easily acted on than a primary. The carboxyl group was not split up. Some experiments were made with urea, uric acid, and hippuric acid, as sources of both carbon and nitrogen, and most of the organisms grew well in these media, as also did the well-known organisms of typhoid, paratyphoid, and dysentery. All the organisms were able to utilise the nitrogen in nitrates and nitrites. J. H. J.

Transformation of Cyanamide into Carbamide by the Microbes of the Soil. P. Mazé, Vila, and M. Lemoigne (*Compt. rend.*, 1919, **169**, 921—923).—It is shown that numerous common species of bacteria abundant in all soils in a good state of cultivation can grow in the presence of cyanamide at a concentration of 1 in 1000, and are capable of rapidly converting the cyanamide into carbamide. W. G.

Solubility of Sparingly Soluble Silver Salts Demonstrated by their Nucleus-destroying Action. H Bechhold (*Kolloid Zeitsch.*, 1919, **25**, 158–161). *Staphylococcus* cultures in agar-jelly were partly covered with filter paper which had been coated with various sparingly soluble silver salts and left for four days in the dark at the ordinary temperature. The preparation was then placed in an incubator for forty-eight hours, and the area was

measured which was entirely free from the micro-organism. It is shown that the areas are practically proportional to the solubility of the salt employed. The experiments were carried out with metallic silver and the oxalate, oxide, carbonate, chromate, chloride, cyanide, thiocyanate, bromide, iodide, and sulphide. Similar experiments were carried out with metallic silver and silver chloride, but using cultures of various micro-organisms, and from the area of the free space deductions are drawn as to the resistance of these organisms to silver and silver chloride. In the case of metallic silver *B. pyocyaneus* is absolutely unacted on, and then follow in decreasing order of resistance, *B. coli*, the organism of swine erysipelas, *Staphylococcus*, paratyphoid, typhoid, and *B. proteus*. In the case of silver chloride the order is entirely different, the organism of swine erysipelas being most resistant, and this is followed in order by *B. pyocyaneus*, *Staphylococcus*, *B. proteus*, *B. coli*, paratyphoid, and typhoid. Except in the case of the organism of swine erysipelas, silver chloride is much more poisonous than metallic silver.

J. F. S.

Further Experiments on the Correlative Formation of Acetaldehyde and Glycerol by the Scission of Sugar, and New Contributions to the Theory of Alcoholic Fermentation. Carl Neuberg and Elsa Reinfurth (*Ber.*, 1919, **52**, [*B*], 1677—1703. Compare A., 1914, i, 118).—As the result of the many investigations carried out by Neuberg and his co-workers in recent years, the following representation of the processes occurring in alcoholic fermentation is given:

I. $C_6H_{12}O_6 - 2H_2O = C_6H_8O_4$, the aldol of methylglyoxal

II. $C_6H_8O_4 = 2CH_2{:}C(OH)\cdot CHO$ or $2CH_3\cdot CO\cdot CHO$.

III. $CH_2{:}C(OH)\cdot CHO + H_2O + H_2 =$ Glycerol + $CH_2{:}C(OH)\cdot CHO + O$ Pyruvic acid.

IV. $CH_3\cdot CO\cdot CO_2H = CO_2 +$ Acetaldehyde.

V. $CH_3\cdot CO\cdot CHO + O =$ Pyruvic acid + $CH_3\cdot CHO + H_2$ Ethyl alcohol.

According to this scheme, methylglyoxal and its corresponding acid, pyruvic acid, are intermediate compounds, and glycerol and acetaldehyde by-products in fermentation. The fact that methylglyoxal may be obtained from sugar by means of quite mild, alkaline agents (A., 1913, i, 1155) is suggestive, and led the authors to investigate the fermentation of sugar in the presence of such substances, especially as it had already been found that the activity of zymase is not impaired by such alkaline compounds (A., 1915, i, 1043). Preliminary experiments showed that the by-products, acetaldehyde and glycerol, become the chief products if sodium sulphite is the agent added (A., 1917, i, 502). This was explained by the formation of the very stable bisulphite compound (A., 1918,

i, 517), the corresponding compounds of dextrose or pyruvic acid being so easily dissociated that the reaction is not stopped until the acetaldehyde stage is reached. Owing to the arrest of the further reduction of the aldehyde, the available hydrogen must attack some other substance, leading, according to the above theory, to increased production of glycerol. This is now known to be actually the case, having by other workers been applied to the technical production of glycerol. In Neuberg's experiments it was found that for every molecule of acetaldehyde produced there is also one molecule of glycerol, the maximum yield of aldehyde being about 73%, and of glycerol about 70%, of that required by the equation $C_6H_{12}O_6 = CH_3{\cdot}CHO + C_3H_5(OH)_3 + CO_2$.

An important confirmation of this theory of the action of the alkaline sulphite is the fact that neutral, insoluble sulphites, like those of calcium, magnesium, and zinc, and mixtures of sodium sulphite with phosphoric acid or sodium dihydrogen phosphate (that is, actually a feebly acid mixture) influence the course of the fermentation in the same way. In fact, the use of calcium sulphite is to be preferred in all such studies. Furthermore, the more dilute the solution is, the less marked is the effect of the sodium sulphite, even if the actual quantity present is 300% of the weight of the sugar.

The earlier experiments were performed with top yeast. The same results, at any rate in the presence of calcium sulphite, are given by bottom yeast, dried yeast, or maceration juice. In fact, the production of acetaldehyde (sodium nitroprusside–piperidine test) may be demonstrated in less than half an hour by incubating a mixture of 20 c.c. of 10% sucrose or dextrose, 2 grams of baker's yeast, and 2 grams of calcium sulphite (made from sodium sulphite and calcium chloride).

Some experiments on the fermentation of the trioses in the presence of calcium sulphite are also described. Dihydroxyacetone yields acetaldehyde, but disproportionate amounts of glycerol, sometimes higher than the expected quantities, whilst glyceraldehyde gives no acetaldehyde at all. J. C. W.

The Course of Alcoholic Fermentation in the Presence of Calcium Carbonate. Johannes Kerb (*Ber.*, 1919, **52**, [*B*], 1795—1800).—Fernbach and Schön (A., 1914, i, 237, 910) reported the production of a large amount of calcium pyruvate during the fermentation of dextrose or invert-sugar in the presence of calcium carbonate, which seemed incredible to the author, since he found that pyruvic acid and its salts are more rapidly fermented by yeast than sugar itself (A., 1913, i, 1026). He has therefore tested the question, and finds that the production of alcohol by pure cultures of yeast is quite normal, and that no trace of a pyruvate is present in the soluble calcium salts formed. These consist of the sulphate, phosphate, hydrogen carbonate, and acetate. The only effect is that the yield of acetaldehyde and acetic acid is slightly greater. It is probable that Fernbach and Schön used an impure ferment which

produced a lactate and then pyruvate, that is, the normal alcoholic fermentation was very much suppressed. J. C. W.

The Course of Alcoholic Fermentation in an Alkaline Medium. II. Fermentation with Living Yeast in Alkaline Solutions. Carl Neuberg and Julius Hirsch (*Biochem. Zeitsch.*, 1919, **96**, 175—203. Compare A., 1917, i, 502).—In the fermentation of sugar by living yeast in the presence of sodium hydrogen carbonate a portion of the acetaldehyde which is formed as an intermediate product is not reduced to alcohol, but is converted into an equimolecular mixture of acetic acid and alcohol. An amount of glycerol equivalent to this portion of acetaldehyde is simultaneously produced. S. S. Z.

The Mechanism of the "Fixation" Method in the Degradation of Sugar into Acetaldehyde and Glycerol. The Correlation of Acetaldehyde and Glycerol during the Entire Process of Fermentation, the Time Factor in this Process and its Relation to Alcoholic Fermentation. Carl Neuberg and Julius Hirsch (*Biochem. Zeitsch.*, 1919, **98**, 141—159).—At every stage during the process of fermentation of sugar in the presence of sodium sulphite, acetaldehyde and glycerol are produced in equimolecular proportions. As ethyl alcohol and carbon dioxide are also produced independently at the same time in equivalent proportions, the fermentation process can be followed by estimating the alcohol and aldehyde at the various stages. S. S. Z.

Utilisation of Amides by Yeast. Pierre Thomas (*Ann. Inst. Pasteur*, 1919, **33**, 777—806).—Under suitable conditions, yeasts are capable of utilising carbamide, and to a lesser extent acetamide, as their source of nitrogen during the fermentation of sugar. Slight utilisation of propionamide and butyramide was indicated. The mechanism of this utilisation is not clear. Although all the experiments with carbamide indicate that the organic nitrogen is converted into ammoniacal nitrogen before utilisation, it was not possible to detect any urease or other such hydrolysing ferment either in the culture liquids or in the expressed cellular juice of the yeast. W. G.

Influence of Zinc Chloride on the Alcoholic Fermentation of Living and Killed Yeast. S. Kostychev and L. Frey (*J. Russ. Bot. Soc.*, 1916, **1**, 39—47; from *Physiol. Abstr.*, 1919, **4**, 416).—Zinc chloride causes a production of acetaldehyde in "hefanol" and dry yeast, but not in living yeast. An important part of fermented sugar forms some compounds the structure of which is not yet known; acetaldehyde is formed only in presence of sugar; the quantity of carbon dioxide exceeds the quantity of alcohol. J. C. D.

The Action of Salts of Zinc and Cadmium on the Ferments of Yeast. S. Kostychev and Zubkova (*J. Russ. Bot. Soc.*, 1916, **1**, 47—56; from *Physiol. Abstr.*, 1919, **4**, 416).—The formation of acetaldehyde by dry yeast under the action of zinc salts depends on the influence of the zinc ion; a similar, but more energetic, effect can be produced by cadmium salts in the case of sugar fermentation, but not in the autolysis in water.

In the presence of cadmium salts, sucrose and lævulose produce a much larger quantity of acetaldehyde than dextrose. The reduction activity of yeast is very strongly inhibited by cadmium; the proteolytic ferments, on the contrary, show no change in their power either in the presence or absence of that metal. Salts of calcium, magnesium, strontium, mercury, aluminium, and antimony give no effects analogous to those produced by zinc and cadmium.

J. C. D.

The Decomposition of Lactic Acid by Killed Yeast. V. I. Palladin and D. A. Sabynin (*Bull. Acad. Sci. Petrograd*, 1916, 187—194; from *Physiol. Abstr.*, 1919, **4**, 417).—Lactic acid is decomposed by killed yeast in the presence of methylene-blue, and in a lesser degree in the presence of pyruvic acid; in the latter case, acetaldehyde is not produced. The authors believe that acetaldehyde plays a rôle of an acceptor of hydrogen, and is transformed into alcohol. Further work is necessary to determine whether lactic acid is an intermediate compound in the course of alcoholic fermentation. J. C. D.

The Influence of Alcohol and Methylene-blue on the Evolution of Carbon Dioxide by Killed Yeast. V. I. Palladin and E. I. Lovchinovskaia (*Bull. Acad. Sci. Petrograd*, 1916. 253; from *Physiol. Abstr.*, 1919, **4**, 416).—The experiments on the capacity of killed yeast to oxidise alcohol to carbon dioxide in the presence of an hydrogen acceptor failed. J. C. D.

The Yeast Saccharomyces Thermantitonum. Hans von Euler and Ingvar Laurin (*Biochem. Zeitsch.*, 1919, **97**, 156—170). —The inversion capacity, the catalase activity, the rate of fermentation at 35° and 40°, and the growth of *Saccharomyces thermantitonum* have been studied. The culture now examined showed certain deviations in its behaviour at the characteristic temperatures from the original culture (1905). It is suggested that adaptation may be responsible for this. S. S. Z.

Rôle Played by Water in the Processes of Alcoholic Fermentation and of Respiration of Plants. V. I. Palladin (*Rec. d'art. dedié au Prof. C. Timiriazev*, 1916, 1—34; from *Physiol. Abstr.*, 1919, **4**, 426).—The replacement of water, although only partial, by some other solvent, such as glycerol, ethylene glycol, formamide, pyridine, or ethyl alcohol, inhibits strongly the activity of zymase, carboxylase, and reductase. In the absence

of water there is no possibility for action of either ferments of alcoholic fermentation or of those of the anærobic phase of respiration. Water is assimilated during respiration, and is used for an anærobic oxidation of dextrose. The total carbon dioxide excreted at the time of respiration is of anærobic origin. Hydrogen, which is formed in higher plants during their respiration as a result of the anærobic decomposition of dextrose, is temporarily adsorbed by some special hydrogen acceptors (respiratory pigments). The total amount of oxygen adsorbed at the time of respiration is used exceptionally to oxidise hydrogen bound by hydrogen acceptors. Water produced during respiration is of anærobic origin. Anthocyanins play no immediate rôle in the respiratory process. Peroxydases serve for the formation of water and of pigments. The respiratory pigments play a rôle of mediators between the products of the anærobic decomposition of dextrose and peroxydases. The oxidation of chromogens follows the scheme of a moist auto-oxidation. Oxygen adsorbed at the time of respiration acts only as a hydrogen acceptor. Thus the majority of cases, if not all, in which the assimilation of atmospheric oxygen is accepted are in reality cases of an oxygen assimilation from water.

J. C. D.

Apparatus for the Study of Photosynthesis and Respiration. W. J. V. Osterhout (*Bot. Gaz.*, 1919, **68**, 60—62).—A very simple apparatus is described and figured in the original, by means of which the air in a closed space, in which is present a branch or twig with green leaves and with the stem dipping into water, is caused to circulate through a solution of an indicator sensitive to carbon dioxide. By means of this the variation in the carbon dioxide concentration in the closed space may be followed, whilst the process of photosynthesis or the process of respiration is proceeding in the plant.

W. G.

Carbon Dioxide and Plants. II. E. Reinau (*Chem. Zeit*, 1919, **43**, 449—451, 489—491, 509—512, 524—525. Compare Klein and Reinau, A., 1914, i, 789).—From a lengthy review of the available data concerning the amount of carbon dioxide in the air, its fluctuations, and its effect on the growth of plants, the author is led to the following conclusions. Brown's theory of the internal pressure of carbon dioxide in plants containing chlorophyll is extended to the phenomena of assimilation under natural climatic conditions, and a mathematical expression is developed which takes into consideration the effect both of water and carbon dioxide on the growth of plants. The differences in concentration of these substances within and without the plant are regarded as differences of tension, the value of which appears to depend mainly on temperature and atmospheric humidity. Under climatic conditions, the amount of assimilation by green plants is not proportional to the absolute carbon dioxide content of the air, but to the difference in tension. The internal pressure of carbon dioxide

depends on the temperature, with rise of which it increases, and also on the illumination, with increase of which it falls. The two functions are explained by Willstätter's conception of the dual nature of chlorophyll; the presence of magnesium in the latter enables it to form a dissociating compound with carbon dioxide resembling a bicarbonate, whilst its chromophoric complex conditions its sensitiveness to light. The actual value of the carbon dioxide tension difference depends on the capacity of the air to receive water vapour, and therefore indirectly on the temperature, and this is explained by the close connexion which exists between the utilisation of the carbon, water, and salts within the plant.

The generally accepted idea that the plant is only able to utilise 0·5—1·0% of the light energy falling on it appears to be erroneous. Assimilation of carbon must proceed simultaneously with the evaporation of water; the latter process requires from 25·5% (in full sunlight) to 92·3% (in shade) of the energy derived from the sun by the leaf; the chlorophyll, in virtue of the power of selective light absorption exhibited by its chromophoric complex, converts about 7% of the light energy into chemical energy, and can utilise this amount completely in experimental cases and to the extent of 10—33% under climatic conditions.

The carbon dioxide content of the atmosphere is regulated by the activity of terrestrial green plants and of the sea on the one hand, and by that of humus (edaphon) on the other; this is rendered probable by the extreme sensitiveness of plants to alteration in the tension of carbon dioxide and by the fact that the action of green plants and "edaphon" is so nicely balanced that the actual quantity of carbon dioxide in the atmosphere is the expression of the dynamic equilibrium of the results of these two factors. Consequently, the absolute carbon dioxide content of the atmosphere is not a measure of the amount of carbon dioxide available for vegetation, but represents the proportion which cannot be lessened by plants under average conditions. It is conceivable that cases could arise in the open in which the plant suffers from too little carbon dioxide; the agricultural aspect of this possibility and the means of preventing it are discussed in the original paper, as is also the beneficent effect of an increased concentration of carbon dioxide on diseased plants.

Schlœsing's theory of the regulation of the carbon dioxide content of the atmosphere by the ocean is regarded as not sufficiently firmly established, and as a partial aspect of the actual case.

H. W.

Formation of Inositol and Hexaldehyde in the Light. P. R. Kögel (*Biochem. Zeitsch.*, 1919, **97**, 21—23).—A theoretical paper. Inositol and hexaldehyde in the plant are formed by photosynthesis according to the following scheme:

Tetrahydroxyethylene —>

hydrate of hexaketohexamethylene —> inositol.

Inositol —> *cyclo*hexanone —> hexaldehyde.

In a previous communication (A., 1919, i, 471) the author put forward a scheme in which he considered that tetrahydroxyethylene was an intermediate product in the formation of formaldehyde from carbon dioxide. S. S. Z.

The Hydrocyanic Acid Question. L. Rosenthaler (*Schweiz. Apoth. Zeit.*, 1919, **57**, 267—270, 279—283, 295—297, 307—313, 324—329, 341—346; from *Chem. Zentr.*, 1919, iii, 274—275).—Dezani's supposed conversion of hydrocyanic acid into ammonia by the sap of plants is erroneous; its production is due to the hydrolysis of the cyanohydrins of sugar, and occurs under conditions which could not obtain in the plant. The author has been unable to detect any formation of ammonia from hydrocyanic acid in the cold, unchanged, and therefore acid, sap from the leaves of *Cornus sanguinea*, *Sambucus nigra*, etc. The presence of hydrocyanic acid, which is important from the point of view of Treub's hypothesis of nitrogen assimilation, has been detected with certainty in about 360 varieties in 148 species and 41 families; the varieties are enumerated in the original memoir, and particular reference is made to the distribution of the acid in the various parts of the plant. Generally, the presence of alkaloids and ethereal oils appears to be incompatible with the presence of hydrocyanic acid. H. W.

Histological Investigations of Oxydases and Peroxydases. G. Marinesco (*Compt. rend. soc. biol.*, 1919, **82**, 258—263; from *Chem. Zentr.*, 1919, iv, 173).—The presence of oxydases in the cells of various tissues can be detected histologically by the blue coloration of the cell granula when treated with solutions of α-naphthol and *p*-phenylenedimethyldiamine. Since, however, fatty substances give a coloration with this reagent, a control with osmic acid and Nile-blue must be made in order to obtain an estimate of the actual amount of oxydase present. The presence of peroxydase can be detected by Perl's iron reaction, since its action is connected with the presence of this metal. H. W.

The Constituents of Wood which give Colour Reactions. III. H. Wichelhaus (*Ber.*, 1919, **52**, [*B*], 2054—2056. Compare A., 1916, i, 874; 1918, i, 151).—The active constituents have been removed from the distillates by extraction with ether and purified by distillation under greatly diminished pressure; two fractions, b. p. 88°/0·4 mm. and 95—105°/0·4 mm., are obtained, together with formic acid. Analyses of the fractions give results in agreement with those required by the formulæ $C_{16}H_{22}O_9$ and $C_{16}H_{22}O_{10}$ respectively, which are simply related to the formulæ of brazilin and hæmatoxylin. H. W.

Some Components of Althæa (Marsh Mallow) Root. Oscar von Friedrichs (*Arch. Pharm.*, 1919, **257**, 288—298).—Marsh mallow root contains 1·7% of an oil, consisting of glycerides of palmitic and oleic acids, together with butyric acid and a phyto-

sterol apparently identical with sitosterol; a hydroxy-acid of high molecular weight also appears to he present. The odour of the root is due to a substance of unknown composition, soluble in ether, insoluble in light petroleum, and non-volatile in a current of steam. The root contains a lecithin in which palmitic and oleic acids occur, and the base of which consists of choline. The sugar present is principally sucrose, of which the root contains 10·2%, the proportion of invert sugar being only 0·78%. The mucilage has the formula $(C_6H_{10}O_5)_n$ and consists of glucosan (64%) and xylan. No galactose is present, but another saccharo-colloid, giving *d*-galactose on hydrolysis, is found. T. H. P.

The Saponins of Chenopodium quinoa, Euphorbia helioscopia (Tithymatus helioscopius), Euphorbia Peplus, and Mercurialis perennis. M. GONNERMANN (*Biochem. Zeitsch.*, 1919, **97**, 24—40).—Preparations of the acid and neutral saponins of these plants have been investigated for their activity by hæmolysis of sheep's and human corpuscles. The titres are given. S. S. Z.

The Saponin in Fenugreek Seeds. H. E. WUNSCHENDORFF (*J. Pharm. Chim.*, 1919, [vii], **20**, 183—185).—The saponin may be isolated by extraction with alcohol and precipitation by ether from the alcoholic solution; the substance consists of a semi-crystalline, white powder, m. p. 214—215°. On acid hydrolysis it yields a sapogenin and dextrose. W. P. S.

Endothia Pigments. II. Endothin-red. L. E. SANDO (*Amer. J. Bot.*, 1919, **6**, 242—251; from *Physiol. Abstr.*, 1919, **4**, 350).—This pigment was obtained from the alcoholic extract of cultures of *Endothia fluens* grown on rice. Analysis and properties indicate a formula C_7H_5O and its probable relationship to the catechol group. J. C. D.

Chemistry of Heterotropic Phanerogams. JULIUS ZELLNER (*Monatsh.*, 1919, **40**, 293—311).—A further extension and elaboration of the author's work on this subject (compare A., 1914, i, 913). Analysis of the ash of *Neottia nidus avis*, *Monotropa hypopitys*, *Cuscuta europaea*, *Lathraea squamaria*, and *Orobanche gracilis* discloses a high percentage of potassium, medium or small amounts of calcium, normal quantities of magnesium, and varying amounts of manganese which are probably connected with the presence of very active oxydases. The ratio of soluble nitrogen to total nitrogen is relatively high, but not the same for all parts of the plant. The question of the osmotic pressure of the cell sap is discussed, but, unfortunately, direct measurement is not yet possible. On various grounds, the author is led to the conclusion that heterotropic plants poor in chlorophyll are richer in osmotically active substances than are the green plants. Analyses show that in all probability the concentrations of cell sap in the parasite and host do not differ widely, in spite of the frequently great differences in water content.

The paper concludes with a critical review of the results obtained by the author and others in the study of the biochemistry of heterotrophic phanerogams. H. W.

The Honey of the Poplar. GEORGES TANRET (*Compt. rend.*, 1919, **169**, 873—874).—The sugary exudation on the leaves of *Populus nigra* contains three sugars, namely, melizitose, dextrose, and lævulose. W. G.

The Colouring Matter of the Red Pea Gall. MAXIMILIAN NIERENSTEIN (T., 1919, **115**, 1328—1332).

Function of Oxalic Acid in the Plant. The Enzymic Degradation of Oxalic Ions. MARKUS STAEHELIN (*Biochem. Zeitsch.*, 1919, **96**, 1—50).—Various plants have been examined and found to contain an enzyme which acts on oxalic ions. It appears that the enzyme is fairly widespread in the plant kingdom, being also present in non-acid plants. It is found in most parts of the plant. The enzyme, which is an oxydase, also functions as a carboxylase converting a part of the oxalic ions into carbon dioxide. Its optimum temperature is 30—40°, and it is destroyed on boiling. It is active under ærobic conditions. In the leaves of *Rumex* the degradation of the oxalic ions proceeds according to the formula of a unimolecular reaction, whereas in the powdered leaves of *Helianthus* it functions in accordance with the law of autocatalysis. Its activity is retarded with increased concentration of oxalates. S. S. Z

Chemical Composition of Natural and Polished Italian Rice. I. GIOVANNI ISSOGLIO (*Atti R. Accad. Sci. Torino*, 1917—1918, **53**, 423—436).—The analytical results obtained by the author show that polished rice is very poor in ash and also in total phosphoric oxide, the phytin phosphoric oxide being reduced to a minimum. T. H. P

Chemical Composition of the Residues from the Treatment of Rice. II. GIOVANNI ISSOGLIO (*Atti R. Accad. Sci. Torino*, 1918—1919, **54**, 440—451).—The rice offals derived from the husk are all very poor in nutritive substances. The residues obtained by removal of the outer cortical layers of the corns are, however, very rich in organic and inorganic phosphorus compounds, fats, and proteins, and contain phytin and vitamines. A third class of residues, composed of small, detached fragments of rice, together with foreign seeds, contains (1) products such as rice embryos, etc., which are used only as cattle feed, and (2) products which are similar in chemical composition to rice and are of value as human food. The results emphasise the necessity of reducing to a minimum the treatment to which rice is subjected. T. H. P